2.5

Nation-wide survey of possible sites for erecting synthetic liquid-fuels plants was begun recently with award by the Army's Engineer Corps of a contract to the firm of Ford, Bacon & Davis, Inc., to make sample studies in western Kentucky, northwestern Colorado, and southeastern Texas. These areas were selected because they have large known supplies of coal, oil shale, and natural gas. The study will be completed in 4–6 mo., and may be continued in other areas of the country where the basic raw materials are known to exist. The survey is not intended to designate specific sites for plants or determine the total coal, natural-gas, and oil-shale reserves of the United States, but merely to determine general areas where the requirements for 1 or more plants can be met.

2523. ———. Future of German Synthetics Industry. Vol. 47, No. 51, 1949, p. 122.

United States, British, and French military governors have agreed on the security limitations to be imposed upon West German industry. The production of synthetic rubber and butadiene is prohibited, and all facilities for producing butadiene at the Hüls, Ludwigshafen, and Leverkusen plants are to be removed or destroyed. The production of styrene is limited to 20,000 tons per year. The production of petroleum, oil, and lubricants directly or indirectly from coal or brown coal by the Bergius hydrogenation process, the Fischer-Tropsch synthesis, or analogous processes also is prohibited except, temporarily, to the extent inseparable from the production of hydrocarbon waxes for the manufacture of synthetic fatty acids for the production of detergents. Production of synthetic waxes is to cease by December 31, 1949, and the 2 Fischer-Tropsch plants engaged in this are to be removed or destroyed at that time. All other Fischer-Tropsch plants are to be removed or destroyed immediately, as are all Bergius plants except that at Wesseling, which is to be retained for refining natural petroleum, for hydrogenating heavy residues from such refining, and for the synthesis of NH_3 and MeOH.

2524. ———. Company Formed in South Africa to Make Petrol From Coal. Vol. 49, No. 26, 1950, p. 46.

South African Coal, Oil & Gas Corp. has been formed in Pretoria to synthesize liquid petroleum products from coal. Erection of the plant, including O_2 manufacture, gasification, synthesis, oil-treatment units, boiler houses, and other units, will be thrown open to private contractors' bids. The Government has guaranteed up to £13,000,000 ($36,400,000). More than £20,000,000 is expected to be needed. The coal to be used is that from the Vredefort district. Production from the plant is not likely for 3 yr.; initial output will include about 1,000,000 bbl. of gasoline per yr.

2525. ———. Refinery to Be Rebuilt. Vol. 49, No. 48, 1951, p. 69.

Reconstruction and expansion into a modern refinery of the war-damaged facilities of Ruhrchemie A.-G. at Oberhausen-Holten has been approved. The new plant will be built around existing distillation and cracking units, and a reformer will be added for improving motor-fuel quality. The completed plant will be able to process about 5,000 bbl. per day, with a cracking capacity of about 2,000 bbl. Koch Engineering Co. of Wichita, Kans., is to build the cracking plant. Another project is the new plant of about 2,000 bbl. per day capacity to be erected at Muelheim on Ruhr by Ruhrbau, G. m. b. H., a company jointly organized by Braunkohle Benzin A.-G. and the Stinnes group. Parts of a shut-down shale-oil retorting plant at Balingen in Wuerttemberg will be used. It is planned to add possibly another 2,000 bbl. per day capacity, as well as cracking units.

2526. ———. Synthesis Plant in Africa. Vol. 49, No. 48, 1951, pp. 70–71.

Construction of the coal-to-oil gasoline-synthesis plant recently announced by the South African Coal, Oil & Gas Corp. Ltd., will be started soon by the M. W. Kellogg Co. The plant will be adjacent to the Vaal River, near Coalbrook in the Orange Free State, about 40 miles south of Johannesburg. The project is an integrated plant, which embraces the opening of virgin coal deposits, construction of aboveground gasification facilities to transform coal to synthesis gas, and the complete synthesis plant to produce liquid hydrocarbons. Kellogg's Synthol process will be utilized. It has been thoroughly developed and tested in the company pilot plant. The Coalbrook coal to be used as the raw material occurs at an average depth of 400 ft., with seams ranging in thickness from 10–20 ft. It is mined at a pithead cost equivalent to less than $1.00 per ton. Operations will be adjusted to produce maximum gasoline and diesel oil rather than chemicals.

Oji, G. *See* abs. 1897, 1898, 1899.

Okamura, T., and Ogawa, S. Magnetic Behavior of Magnetite at Low Temperatures. II. *See* abs. 2299.

Oketani, S. *See* abs. 3439, 3440, 3440a.

Okuna, T. *See* abs. 2501.

2527. Olmer, F. [Reduction of Iron Oxides by Carbon Monoxide in the Presence of Certain Natural Impurities.] Compt. rend., vol. 206, 1938, pp. 353–355; Chem. Abs., vol. 32, 1938, p. 2447.

Although CO is unstable at 20°–1,000°, the velocity of the reaction $2CO = CO_2 + C$ is very small in the absence of a catalyst. In the presence of Fe_2O_3 above 350°, it occurs rapidly either alone or accompanied by reduction of the Fe_2O_3, the velocity being proportional to the mass of the catalyst. Fe alone acts similarly. Similar experiments with Fe_2O_3, containing a phosphate or aluminate show that P_2O_5 and Al_2O_3 hinder the catalytic action of the Fe (or Fe_2O_3).

2528. ———. [Reduction of Iron Oxides in the Presence of Foreign Substances.] Rev. mét., vol. 38, 1941, pp. 129–134; Chem. Abs., vol. 36, 1942, p. 6931.

Reduction of Fe compounds was studied by photographically recording pressure drop of a constant volume of a reducing gas, after adsorption of H_2O and CO_2 formed during the reaction. The powdered sample was reduced in a fused SiO_2 chamber in a resistance furnace, regulated by an auxiliary nichrome-wound furnace. Reduction of Fe_2O_3 with H_2 begins around 325° and continues until pure Fe is formed, without intermediate formation of FeO. For an oxide simply dried at 300°, reduction begins at 240°; for an oxide that has been calcined at 1,300°, at least 400° is required. In the first case, Fe_3O_4 is formed at 300°; in the second, no Fe_3O_4 is formed. The decomposition of CO in the presence of different Fe compounds was studied to determine catalytic reactions, if any. No decomposition takes place with CO lower than 45%. For greater CO concentrations than 55%, catalysis is very pronounced. Fe_2O_3, Fe_3O_4, and cementite have no catalytic effect on the decomposition of CO. No FeO is produced by CO reduction. Catalysis of CO decomposition with about 20 metals and oxides was studied. Cu, Pb, Zn, and Sn oxides are reduced quantitatively; oxides of W and Mo only partly even at 1,000°; Al_2O_3 and Cr_2O_3 are unaffected. Only oxides of Fe, Co, and Ni show a pronounced drop in gas pressure and a heavy C deposit; only these are decomposition catalysts. Experiments were conducted to show the relation between catalytic properties and magnetism of metals. The catalytic effect is believed to be connected with surface absorption, which depends on the radius of curvature of catalyst particles. The velocity of catalysis by Fe increases up to 580°. It appears that the reduced Fe is in a state of very fine division, and, at 580° these particles agglomerate; this increases the radius of curvature. Dilution of the powdered Fe with an inert substance prevents agglomeration and preserves catalytic activity independently of temperature.

2529. ———. Decomposition of Carbon Monoxide by Ferromagnetic Metals. Jour. Phys. Chem., vol. 46, 1942, pp. 405–414; Chem. Abs., vol. 36, 1942, p. 3092.

Catalytic decomposition of CO at temperatures below 1,000° is limited to Fe, Ni, and Co, though there is no apparent relation between catalytic activity and magnetic properties. The activity is due to the metals, and not to their compounds, since there is no decomposition outside of the range at which the metallic phase exists. The activity curve for the pure metal passes through a maximum at 580°–590°, owing to agglomeration of the particles of the catalyst, thereby reducing their effective surface. At higher temperatures the speed of reatcion rises again and then drops toward zero as the temperature is approached at which CO is stable. If the catalyst is mixed with an inert substance that will prevent agglomeration, there is no loss in activity beyond 590°.

2530. ———. Reduction of Fe_2O_3 by Hydrogen. Jour. Phys. Chem., vol. 47, 1943, pp. 317–325; Chem. Abs., vol. 37, 1943, p. 6184.

Kinetic method developed by Olmer (abs. 2528) is applied.

2530a. Onda, K. Effect of an Electric Field on the Synthesis of Hydrocarbons. I. Effect of Voltage. II. Effect of Various Reaction Temperatures. Jour. Soc. Chem. Ind. (Japan), vol. 47, 1944, pp. 641–643, 643–644; Chem. Abs., vol. 46, 1952, p. 7,032.

I. Synthesis was performed with a Co–kieselguhr catalyst. The mean molecular weight of the oil obtained increased with increasing voltage. The I value was independent of the voltage up to 6,000 volts but decreased at 8,000 volts. HCHO formation increased with increasing voltage. The ratio of CO reacted to that of H_2 increases with increasing voltage. II. The mean molecular weight decreased with rising temperature. The I value of the oil was independent of the temperature. HCHO formation increased with temperature.

O'Neill, W. E. *See* abs. 44.

Opitz, W. *See* abs. 1991.

Orchin, M. *See* abs. 888, 3122, 3275a, 3650, 3651, 3652, 3653, 3654, 3655, 3655a, 3655b, 3656, 3656a, 3656b, 3656c.

2530b. Orchin, M., and Schroeder, W. C. Hydroformylation. Unit Processes in Organic Synthesis, by P. H. Groggins. McGraw-Hill Book Co., New York, 4th ed., 1952, chap. IX, pp. 555–595.

Review.

2531. Oriel, J. A. Report on Visit to Oil Targets in the Ruhr and Hanover Areas. Nat. Petrol. News, vol. 37, 1945, R, pp. 926, 928, 930; TIIC Rept. 3; CIOS Rept. XXIII–16, 1945, 23 pp; TOM Reel 198; PB 282.

Plant to use the Oxo process was virtually completed at the Fischer-Tropsch installation at Holten when the war ended. This plant was to treat C_{12}–C_{17} olefins, converting them first to aldehydes by passing them, together with S-free water containing 39 parts of CO to 45 parts of H_2 over the ordinary Fischer-Tropsch catalyst, the temperature in the 1st stage being 135° and the pressure 150 atm., the temperatures being controlled by means of steam pressure. The process was intermittent, each cycle taking 20 min. The Fischer-Tropsch catalyst consisted of 100 parts Co; 5, Th; 8, Mg; and 180–200, kieselguhr. A suggested Fe catalyst was to consist of 100 parts Fe; 2.5–4, Cu; 10, lime; and 15, Kieselguhr; it was made from nitrates by precipitation with CO_2. The aldehydes after distillation were then passed together with pure H_2 over a Ni catalyst to convert them into alcohols. The temperature was 180° and the pressure the same as for the 1st reaction. The alcohols were to be used for making sulfonic soaps. The development work included the dehydrogenation of C_{16}–C_{18} cuts from Fischer-Tropsch operations to olefins for use in the Oxo process. The catalyst in this case was ThO_2 and Cr_2O_3. Describes method of preparing this catalyst.

2532. Orlov, G. [Preparation of Ethylene From Carbon Monoxide and Hydrogen.] Ber. deut. chem. Gesell., vol. 42, 1909, pp. 893–895; Jour. Russian Phys.-Chem. Soc., vol. 40, 1908, pp. 1588–1590; Chem. Zentralb., 1909, I, p. 735; Chem. Abs., vol. 3, 1909, p. 1400.

Coke, in pieces the size of hazelnuts, was soaked in $Ni(NO_3)_2$, dried, and ignited. It was then treated in the same manner with $PdCl_2$ and was finally reduced in a Cu tube by means of MeOH vapor. When a mixture of H_2 and CO is placed over the prepared coke at 95°–100°, the issuing gas consists of CO, $H_2C_2H_4$, and air; CH_4 is not formed. When CO_2 is substituted for CO, neither C_2H_4 nor CH_4 is obtained, but at higher temperatures, or in contact with reduced Ni alone, both of these gases are produced.

2533. Ormandy, W. R. Oil From Coal. Jour. Inst. Fuel, vol. 7, 1933, pp. 71–79; Chem. Abs., vol. 28, 1934, p. 3873.

Review of the production of oil from coal by: (1) Straight distillation over a wide range of temperatures; (2) direct hydrogenation; (3) the distillation of coal and the conversion of the coke into water gas, which is, in turn, converted to oils.

2534. Ormandy, W. R., and Burns, J. Production of Oil From British Coal. Trans. Inst. Marine Eng., vol. 45, 1933, pp. 239–254; Petrol. Times, vol. 30, 1933, pp. 551–552, 579–581, 607–608; Colliery Guard., vol. 147, 1933, pp. 749–751; Chem. Abs., vol. 28, 1934, p. 620.

Quality of oils from coal is discussed with reference to price competition with petroleum. The production of oil from coal is considered under the headings (1) distillation with variation in temperature, (2) hydrogenation, and (3) distillation of coal and conversion of coke into water gas, which by catalytic reactions is converted into a wide range of products. Compares fuel-oil and coal-oil mixtures. Discusses Cunard process of using finely divided coal suspended in oil.

Orochko, D. I. *See* abs. 2169.

2535. Orsoni, B. [Utilization of Synthetic Ammonia Plant for Production of Methanol.] Chimica e industria (Milan), vol. 29, 1947, pp. 137–139; British Abs., 1949, B, I, p. 199.

Details of the preparation of the reaction-gas mixture and of the necessary adaptation of the NH_3 plant equipment to the synthesis of MeOH. The method of preparation of the gas mixture depends on the process in operation for making NH_3. If the H_2 is obtained from water gas, this need be only partly converted to eliminate S as H_2S. The required $CO:H_2$ ratio can be attained by regulating the steam. A small amount of residual CO_2 helps to promote the synthesis of MeOH, thus economizing in water for washing the gas mixture. The water may contain 0.6–0.7 cc. CO_2 per m.³ This offers an advantage over the requirements of NH_3 synthesis. When the CO, CO_2, and H_2 content of the gases reaches about 70–75% in the catalytic cycle, the residual gas must be freed from N_2 and CH_4, preferably by fractionation in the NH_3 plant. This involves the consumption of about 0.25 kw.-hr. per kg. of MeOH, but it can be avoided if O_2, which is always available in an NH_3 plant, is used for the production of water gas (about 0.5 m.³ O_2 is required per kg. of MeOH). For pressures of 2.5–25 atm., steel pipes must be plated (against corrosion by CO) with Zn and other surfaces with Sn; 6% Cr–V–Mo or Cr–Ni steel should be used when higher pressures are applied.

2536. Osborne, R. M. Adsorption of Low-Boiling Hydrocarbons by Activated Carbon. FIAT Tech. Bull. T–34, May 1, 1947, 2 pp.

Carboraffin, which is made from sawdust, activated by $ZnCl_2$, and powdered, is 1 of the several active carbons mentioned in FIAT Final Report 863, and manufactured by the I. G. Farbenindustrie, Leverkusen. It is said to have good adsorptive capacities for low boiling hydrocarbons. A carbon based upon the Carboraffin type with similar adsorption isotherms has now been developed into an active carbon capable of being fluidized and used in a continuous adsorption process. The exact method of manufacture has not been disclosed. On an industrial scale, there have been no developments on the preparation of active carbons that show selectivity for chemical types of hydrocarbons, although on a laboratory scale, where the time factor is not essential, some work has been done. It is almost certain that the presence of metals does not increase the selectivity of a given activated carbon for a particular type of hydrocarbon. Presents some of the physical properties and constants of active carbons developed by the Lurgi Co.

2537. ———. Extraction of Fatty Acids From Dilute Aqueous Solutions From the Fischer Process. FIAT Tech. Bull. T–35, May 1, 1947, 1 p.

Hoesch Benzin plant at Dortmund has been recovering the oxygenated products in the water layer condensed from the Fischer-Tropsch process. This plant operated at medium pressure (7 atm.) with the Co catalyst at 200° and treated about 150 m.^{3} of the condensation H_2O per day. The solution 1st made alkaline to prevent corrosion, was distilled to give an approximately 30% alcohol solution in the overhead; the alcohols range from ethyl to octyl. The ethyl, propyl, and butyl alcohols were separated, and the higher alcohols were sold to the lacquer trade. The bottoms of the distillation were acidified with H_2SO_4 to a pH of 5, and the free fatty acids, corresponding to about 0.4% of the total primary synthesis product, were extracted with naphtha. About 200% naphtha based on the water was circulated. This extracted only the C_4 and higher acids. The recovered acids, amounting to about 1 ton per day, found use in boring oil. Degussa developed a method of extracting lower fatty acids from dilute solutions using ethyl acetate.

2538. Osborne, T. M. Coal-Gasification Unit Completed at Missouri Gas-Synthesis Plant. Southern Power and Ind., vol. 67, No. 7, 1949, pp. 72–73; Chem. Abs., vol. 43, 1949, p. 6393.

New plant for the production of synthesis gas by the steam and O_2 gasification of powdered coal is described briefly. This gas will be washed and cooled and then passed through electrical precipitators to remove dust before being compressed and purified.

Oshima, T. *See* abs. 1892, 1915.

2539. Oshima, Y. High-Pressure Chemical Industries in Japan. Trans. World Power Conf., Chem. Eng. Cong., 1936, 10 pp.; Chem. Abs., vol. 31, 1937, p. 3167.

Development and present status of the synthetic MeOH and NH_3 and compressed gas industries are discussed briefly with special emphasis on plant capacity, economics, and regulatory measures.

2540. Ostermeier, L. [Use of the Residual Gas From the Fischer-Tropsch Gasoline-Synthesis Process as City Gas.] Gas u. Wasserfach, vol. 81, 1938, pp. 52–57; British Chem. Abs., 1938, B, p. 243; Chem. Abs., vol. 32, 1938, p. 3126.

High purity of the residual gas from the Fischer-Tropsch process is an important factor in considering its use for city gas, but this is partly balanced by its high content of inerts, especially CO_2 and high specific gravity. This gas may be converted into city gas by washing out CO_2, preferably with a solution containing a mixture of K and Na carbonate or by detoxification (removal of CO) before removing CO_2. In either case the density and inert content will be reduced to permissible limits, and a mixture of treated and untreated gas may be used, with or without other normal manufactured gases. The combination of synthesis-gas manufacture with the use of the residual gas would seem to be favorable for large gas works in Germany.

2541. Osterrieth, J. R., and Dechamps, G. Production of Organic Compounds From Coke-Oven Gas. Gas Jour., vol. 201, 1933, pp. 202–206; Gas World, vol. 98, No. 2531, coking sec., 1933, pp. 14–17; Chem. Abs., vol. 27, 1933, p. 1736.

Commercial methods for producing MeOH and the higher alcohols from the constituents of coke-oven gas.

2542. Ostwald, W. [Synthetic Fuels.] Motorwagen, vol. 28, 1925, pp. 565–567.

Bergius and Badische processes.

2543. ———. Motor Fuels From Cheap Materials. Oil Gas Jour., vol. 24, No. 38, 1926, p. 136; Chem. Abs., vol. 20, 1926, p. 2572.

Discussion of the production of synthetic motor fuels by the Mittasch, Fischer, Zelinsky, and Bergius processes. A synthetic fuel containing Fe carbonyl as an antidetonating component is not as poisonous as $Pb(C_2H_5)_4$, but when used in engines, it causes the valves to become incrusted quickly.

2544. ———. [Influence of German Gasoline Chemistry Upon American Refinery Technology.] Kraftstoff, vol. 16, 1940, pp. 271–273; Chem. Abs., vol. 35, 1941, p. 8268.

Present developments are traced to I. G. Farbenindustrie A.-G., high-pressure hydrogenation, and Fischer low-pressure synthesis. Shows schematic interrelations of the various processes.

2545. Ota, N. Water Gas by the Reaction of Methane and Carbon Dioxide. I. Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 284–290; Chem. Abs., vol. 43, 1949, p. 1944.

Equivalent mixture of CH_4 and CO_2 under atmospheric pressure was passed through a layer of catalyst at 700°–800° to obtain CO and H_2. Catalysts composed of Ni and various oxides and carriers in different ratio were used, and, among those tried, 1 containing Ni, MgO, and kieselguhr in the ratio 1 : 1 : 4 gave the best yield of $CO+H_2$ at 700° with the least formation of C on the catalyst.

2546. ———. Water Gas by the Reaction of Methane and Carbon Dioxide. II. Methods of Preventing Carbon Formation on the Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 284–290; Chem. Abs., vol. 43, 1949, p. 1944.

Formation of C on catalysts can be prevented not only by selecting a suitable catalyst but by (*a*) elevating the reaction temperature, (*b*) taking excess CO_2, or (*c*) adding H_2O to the reacting gas. Thus, when 30% excess CO_2 is used with the CH_4, the reaction proceeds smoothly at 800° with a Ni-kieselguhr catalyst without any other admixture. Similar results were obtained with a gas having 30% H_2O (based on CH_4) at 700° or 10% H_2O at 800°. By adding H_2O, the amount of CH_4 decomposed is increased.

Otto, K. V. *See* abs. 1206.

Otts, K. *See* abs. 2740.

Owens, M. L. *See* abs. 2094.

P

Pace, B. S. *See* abs. 810.

2547. Pace, J., and Taylor, H. S. Velocities of Adsorption of Hydrogen and Deuterium on Hydrogenation Catalysts. Jour. Chem. Phys., vol. 2, 1934, pp. 578–580; Chem. Abs., vol. 28, 1934, p. 6606.

Velocities of adsorption of H_2^1 and of H_2^2 are identical on Cr_2O_3, $ZnO–Cr_2O_3$ and Ni supported on kieselguhr, at 110°, 132°, and 184°. This process is, therefore, independent of the difference in zero-point energies, of the rate at which the gas molecules strike the surface, and of an activated migration.

Pacheco, J. R. *See* abs. 2137, 2917.

2548. Padovani, C. [Progress in Production and Synthesis of Fuels.] Giorn. chim. ind. applicata, vol. 7, 1925, pp. 202–210; Chem. Abs., vol. 20, 1926, p. 3225.

Topics considered are: Benzine from petroleum, benzine from sources other than petroleum, light oils from solid fuels, indirect hydrogenation of C, fluidification of C by various chemical processes, liquid fuels from vegetable substances, synthetic petroleum.

2549. ———. Direct and Indirect Use of Methane as Motor Fuel. Proc. World Petrol. Cong., vol. 2, 1933, pp. 795–798; British Chem. Abs., 1934, B, p. 996.

Possibility of using compressed CH_4 as motor fuel, or of converting it into liquid fuel, for example, by direct thermal treatment or by conversion into a mixture of CO and H_2, which would then serve as the raw material for the synthesis of alcohols or light hydrocarbons, is discussed with particular reference to conditions in Italy.

2550. ———. [Treatment of Combustile Gases.] Jour. usines gaz, vol. 58, 1934, pp. 2–7; Chaleur et ind., vol. 15, 1934, pp. 461–468; Chem. Abs., vol. 28, 1934, p. 3872.

Lecture reviewing experiments on the conversion of CO, CO_2, and H_2 to CH_4. By the use of pressures around 10 atm., temperature below 400°, yields of 85–90% in the reaction $CO+3\ H_2=CH_4+H_2O$ can be obtained by the use of a complex (Ni-containing) catalyzer resistant to the effects of normal industrial gas. CO_2 is formed in a side reaction; no C is separated out. The process is important for the manufacture of nontoxic gas of high heating value from inferior fuels. A loss in the reaction of some 25% of the total heating value can be partly recovered. Reviews application of reverse reaction at 800°–900°.

2551. ———. [Conversion of Methane Into Liquid Fuels.] Kraftstoff, vol. 18, 1942, pp. 81–85; Brennstoff-Chem., vol. 23, 1942, p. 207; Chem. Zentralb., 1942, II, p. 971; Chem. Abs., vol. 37, 1943, p. 5217.

Gas mixture from the catalytic conversion of CH_4 according to the equation: $2\ CH_4+O_2=2\ CO+4\ H_2+17.4$ cal. is directly suitable for the synthesis of hydrocarbons by the Fischer-Tropsch process or for MeOH, the latter of which only is of interest to Italy at the present time. The main difficulties in the 1st stage of CH_4 conversion are the lack of suitable mechanically and thermally resistant catalysts, the problem of temperature regulation and the avoidance of side reactions, particularly in the preheating of the gases. The process, as developed, comprises, in addition to the preparation of the catalyst, the special conditions essential for the preheating of the reaction gases before their entrance into the reaction zone, the maximum temperature about 950°. The permissible velocity is about 500 m.^{3} of CH_4 per hr. per m.^{3} of catalyst. From 1 m.^{3} of 95% CH_4, about 1.1 kg. of MeOH (98–99%) can be obtained with a consumption of 0.493 m.^{3} of O_2 and 0.9 kw.-hr., corresponding to the use of 2.85 m.^{3} of synthesis gas (65.2% H_2 and 32.1% of CO), 0.493 m.^{3} of O_2, and 0.10 kw.-hr. The economy of the process is discussed, particularly as regards the supplies of CH_4. With the existence of larger amounts of CH_4, the MeOH process would offer the best solution. It is possible also that the benzine synthesis would be economically successful. The chemical conversion of CH_4 is at present made difficult by the relatively small amounts available, the uncertainty of the amount of reserves, and the present necessity of making quick use of the available supplies and, if necessary, moving the plants from one place to another.

2552. ———. [Evaluation of Italian Solid Fuels.] Chim. ind. agr. biol., vol. 18, 1942, pp. 79–84; Chem. Zentralb., 1942, II, p. 849; Chem. Abs., vol. 37, 1943, p. 5218.

Coal fields in Italy are usually small, widely separated, and of low value. An endeavor has been made to use the poorer coals for local chemical industry in special furnaces or gas producers. Low-temperature carbonization has replaced direct combustion when tar yields and coke properties are satisfactory. When the semicoke is unsatisfactory, the coal is gasified in producers, with tar recovery. A special demand has been noted for producers that give a mixture of CO and H_2 suitable for synthesis. There is a great need for the erection of Fischer plants using Italian brown coal.

———. *See* abs. 2106.

2553. Padovani, C., and Bayan, S. [Reduction of Ferric Oxide With Mixtures of Carbon Monoxide and Hydrogen.] Ann. chim. applicata, vol. 24, 1934, pp. 394–409; Chem. Abs., vol. 29, 1935, p. 419.

Influence of time of contact on the reduction of Fe_2O_3 made from calcined siderite, by a mixture of CO and H_2, in the same proportions as in water gas, has been studied. A phase of complete combustion was noted, which is independent of the velocity or time of contact, within the limits used (temperature 950°), and which ends abruptly when a definite percentage (44.8) of the available O_2 from the Fe_2O_3 is consumed.

2554. Padovani, C., and Franchetti, P. [Reactions of Methane With Mixtures of Steam and Carbon Dioxide.] Inst. Ind. Chem. Fuels, Polytechnicum, Milan, vol. 4, 1932–33, pp. 173–191; Chem. Abs., vol. 29, 1935, p. 1229.

Mixtures of CH_4, CO_2, and H_2O are passed over Ni catalysts, with or without Cu or Al_2O_3 at temperatures from 650° to 1,200°, and principally at 850°. The CO and H_2 formed are measured. The results obtained are compared with those of Fischer and Tropsch (*see* abs. 1025), and Hawk, Golden, Storch, and Fieldner (*see* abs. 1370).

2555. ———. [Incomplete Oxidation of Methane With Oxygen and Air.] Giorn. chim. ind. applicata, vol. 15, 1933, pp. 429–432; Chem. Abs., vol. 28, 1934, p. 2853.

Reaction $CH_4+\frac{1}{2}O_2\rightarrow CO+2H_2+8$ cal. is influenced markedly by the presence of catalysts such as Ni; for example, at 850°–950° with a space velocity of 500, virtually equilibrium conditions were obtained. At 900°, less than 1% CH_4 remained in the reaction product. CH_4 from petroleum cracking, as well as from illuminating gas, was used. With reduced cost of O_2, the above reaction may become of interest in preparing H_2, NH_3 and alcohols.

2556. ———. [Methane Synthesis From a Mixture of Carbon Monoxide and Hydrogen.] Acqua e Gas, vol. 24, 1935, pp. 57–61; Chem. Zentralb., 1936, I, p. 478.

Synthesis of CH_4 under about 10–12 atm. pressure from a synthetic mixture of CO and H_2 (obtained by the gasification of brown coal with O_2 at low temperatures) can be attained up to about 90% at 330° over a Ni catalyst deposited on kieselguhr and activated with Al and Mn at a space velocity of 1,040 and almost complete at lower space velocity. By using illuminating gas to which H_2 had been added, poisoning of the catalyst gradually took place, but after regeneration, it resumed operation so that finally 27% of the CO was converted into CH_4. A partial substitution of the Ni by a natural siderite gave good results with the illuminating gas+H_2. With illuminating gas alone, however, destruction took place through separation of C. A Ni catalyst on active C with illuminating gas+H_2 gave good results, but without H_2 it failed rapidly. High pressures (85–104 atm.) caused the catalyst to fail quickly and promoted the deposition of C.

2557. ———. [Synthesis of Methane From Mixtures of Carbon Monoxide and Hydrogen.] Atti cong. nazl. chim. pura applicata, 5th Cong., Rome, 1935, part II, 1936, pp. 818–828; Chem. Zentralb., 1937, I, p. 2307; Chem. Abs., vol. 31, 1937, p. 7393.

Experiments with various catalyzers containing Ni, Mn, Al, Fe, and Mg all tend to show the superiority of Ni as the catalyzer base.

2558. Padovani, C., and Giordano, I. [Production of Gas With High Hydrogen and Low Carbon Monoxide Contents by the Action of Steam on Carbon.] Acqua e Gas, vol. 9, 1931, pp. 65–81; Chim. et ind., vol. 26, 1931, p. 1064; Chem. Abs., vol. 26, 1932, p. 1417.

Theoretically, the reaction of the production of H_2 is $C+2H_2O=CO_2+2H_2-19$ cal.; but, in practice, the process is carried out in 2 stages according to $C+H_2O=CO+H_2-29$ cal. and $CO+H_2+H_2O=CO_2+2H_2+10$ cal., the second stage being carried out at 400°–500° in presence of a catalyst. From a theoretical application of the law of mass action to the equilibria $CO_2+C\rightleftharpoons 2CO$ and $CO+H_2O\rightleftharpoons CO_2+H_2$ and a study of the ratios $CO:H_2$ and $(H_2O+H_2):H_2$ (the 1st measuring the impurity of the H_2 produced and the 2d the excess of undecomposed steam), considerable divergence was found between theoretical results and those obtained in practice, which is attributed to the thickness and nature of the layer of coke and to the treatment to which it was subjected during the coking process. Methods also were studied of increasing the reactivity of the C: (1) By addition of catalysts (chiefly alkali or alkaline earth salts, or oxides of Fe, Cr, or Mn); (2) by using coke (or more exactly semicoke) prepared under special carbonization conditions. The experimental set-up used in the investigation is described.

2559. Padovani, C., and Lotteri, A. [Reaction Velocities at Low Temperatures in the Water-Gas Equilibrium.] Studi ric. comb., vol. 6, 1936–1937; Jour. Soc. Chem. Ind., vol. 56, 1937, pp. 391–395T; British Coal Utilization and Research Assoc., Monthly Bull., vol. 2, 1938, No. 11, abs. 2342; British Chem. Abs., 1938, B, p. 13; Chem. Abs., vol. 32, 1938, p. 1170.

Composition of the feed was H_2, 46.5; CO, 52.5; N_2, 1.0%; trace of O_2; and no CO_2 or C_nH_m. The catalyst had an Fe_2O_3 basis (commercial). The apparatus is shown. The temperature of the reaction chamber was kept at 400° and that of the preheater was carried at 400°, 520°, and 580° at atmospheric pressure, and a $H_2C:CO$ ratio of 1.87 was used. The velocity coefficient k_1 for the reaction $CO+H_2\rightarrow CO_2+H_2$ was calculated from: $k_1dt=dx/(ax^2+bx+c)$; where t=reaction time and x concentration of CO. At preheater temperatures of 400°, 520°, and 580° the values of k_1 obtained were 0.00509, 0.00732, and 0.00860, respectively. Experiments on the effect of pressure showed that the highest yields lie between 10 and 20 atm. The effect or $H_2O:CO$ ratio was investigated, and it was shown that in order to obtain absolute yields above 90% at 400° a large excess of H_2O is necessary (ratios of 3–4 and space velocities not greater than 300–400). Experiments also are reported for catalytic temperatures of 300°, 350°, 400°, 450°, and 500° with equalized preheater temperature. The variation of k_1 as a function of temperature could be expressed by $k_1=9.38T^2\times 10^{-7}-5.9197T\times 10^{-4}+0.09384$. With a $H_2O:CO$ ratio of 2, high yields are possible only at 450°–500°. With space velocities of about 500, yields of 75–80% can be realized. At 350°–400°, yields of 30–60% only are possible with space velocities between 300 and 500, and at 300° the reaction velocity is definitely too low.

2560. Padovani, C., and Salvi, G. [Oxidation of Paraffin.] Riv. combustibili, vol. 2, 1948, pp. 231–244; Fuel Abs., 1949, No. 2, p. 931; Chem. Abs., vol. 43, 1949, p. 4000.

Some doubtful factors in this process have been studied and improvements and simplifications applied especially in the separation of the oxidation products. A commercial crystallized paraffin, m. p. 50°–52°, was taken as the raw material. The optimum temperature of reaction was found to lie between 130° and 135°. Although the reaction is exothermic, heat had to be applied at certain stages of the reaction to compensate for heat lost by dispersion. Best results were obtained with a $KMnO_4$ catalyst (0.2–0.5%). At the end of the process this catalyst had combined to 80% with the water-soluble fatty acids. 15% of O_2 mixed with the air used as oxidizing agent reduced the reaction period from 16–9 hr., the amount of air required from 480–250 l., and the oxy acids in the final products from 7 to 4%. Al and oxidized Al were found to be the best construction materials for the pilot plant equipment, since they darkened the color of the products least and appeared to have a slight accelerating effect. Whereas the Germans separated the oxidized products by saponification and removed the unsaponifiable matter by distillation under pressure, selective solution was adopted as being simpler and more economical. Two solvents were tested in the laboratory, isopropanol and MeOH–H_2O. Chromatographic separation also was tried, but difficulties were encountered.

Paleari, C. *See* abs. 2706b.

2561. Palfray, —. [Catalytic Hydrogenation Under High Pressures.] Cours conf., No. 1320, March 1945, 18 pp.; Chaleur et ind., vol. 28, 1947, p. 8D.

Study of the catalytic fixation of H_2 on unsaturated bonds, in particular of the synthesis of MeOH and the manufacture of synthetic gasoline. Light or heavy hydrocarbons are converted into light gasoline or lubricants.

Palm, J. W. *See* abs. 3726.

Palmer, H. F. *See* abs. 3218.

Panina, A. M. *See* abs. 1592.

Panning, G. *See* abs. 3137.

Pantazoplos, G. *See* abs. 888.

Pantazoplos, P. *See* abs. 888.

2562. Paranjpe, V. G., Cohen, M, Bever, M. B., and Floe, C. F. Iron–Nitrogen System. Jour. Metals, vol. 188, No. 2, Trans., 1950, pp. 261–267; Chem. Abs., vol. 44, 1950, p. 3423.

Fe–N system was investigated by X-ray diffraction measurements and a controlled nitrogenizing method. The latter is an innovation and depends on the relation between the nitrogenizing power of an NH_3–H_2 mixture and the N content of the Fe–N alloy produced. Clarifies several controversial features of the Fe–N phase diagram.

2563. Pardun, H. [Dependence of the Yield of Fatty Acid Upon the Stage of Oxidation of Aliphatic Hydrocarbons.] Fette u. Seifen, vol. 48, 1941, pp. 397–403; Chem. Abs., vol. 37, 1943, p. 2918.

Fischer-Tropsch slack wax was oxidized in an apparatus at a constant temperature (±1°) and with a uniform current of air. In various experiments 600 l. of air per hr. was blown through 6,000 gm. of slack wax for 1–9 hr. in the presence of 30 gm. Mn stearate as catalyst and at temperatures of 100°–160°. At different stages of oxidation (when the acid numbers were 20, 40, 60, 80, etc.), 40-gm. portions were removed and analyzed for unsaponifiable, fatty acids, OH acids, and nonvolatile soluble acids. From these data and from yields of nonvolatile oxidate obtained in blank runs, interpolation formulas were derived that could be used to calculate the course of oxidation for practical purposes and especially to determine the most favorable stage of oxidation.

2564. Pardun, H. [Edible Fat From Coal.] Seifen-Öle-Fette-Wachse, vol. 74, 1948, pp. 25–27, 49–52; Chem. Abs., vol. 42, 1948, p. 8364.

Review of production of fats by the Fischer-Tropsch hydrocarbon synthesis, oxidation of hydrocarbons to fatty acids and their separation, esterification, and refining of crude triglycerides.

2565. ———. [Distribution of the Fatty Acids Formed by the Oxidation of Paraffins in the Fischer-Tropsch Process.] Fette u. Seifen, vol. 52, 1950, pp. 290–295; Chem. Abs., vol. 44, 1950, p. 10352.

Influence of the degree of oxidation on the distribution of the fatty acids formed in the Fischer-Tropsch process was investigated by oxidizing samples of a paraffin fraction b.$_{13}$ 168°–233° at temperatures of 110°, 120°, 130°, and 140° so as to yield products of acid numbers 10, 20, 40, and 80. The fatty acids were isolated as the Me esters, fractionated, hydrolyzed and analyzed. The distribution of the fatty acids formed a maximum in all cases. With decrease in degree of oxidation this maximum migrates toward fatty acids of higher molecular weight. It is probable that the primary reaction takes place at the end of the paraffin chain, and that the higher-molecular compounds formed first are split further on continuing oxidation.

2566. Pardun, H., and Kuchinka, R. [Influence of the Amount of Air Upon the Oxidation of Paraffin Hydrocarbons.] Fette u. Seifen, vol. 49, 1942, pp. 441–446; Brennstoff-Chem., vol. 23, 1942, p. 208; Ind. Chemist, vol. 21, 1945, p. 447; Chem. Abs., vol. 37, 1943, p. 5697.

To determine the optimal amount of air for oxidation of aliphatic hydrocarbons to acids in liquid phase, a Fischer-Tropsch-Gatsch substrate was oxidized at temperatures 100°–160° with 0.05–1 l. of air per gm. per hr. until an acid No. of 50 was attained. At each temperature, the rate of oxidation rises until a limiting value is reached and then remains constant. The applicable equation is: 1 gm. $D=at-b$, where D=l. of air per gm. of substrate per hr., a=0.03, b for maximum rapidity=4.3, for maximum yield of acids=4.6. The temperature coefficient for 110°–140° is virtually constant at 2.52. Above this temperature it falls to 0.80–1.70.

2567. Paris, A. [Mild Oxidation of Methane Under Pressure.] Chim. et ind., Special No., April 1934, pp. 411–420; Brennstoff-Chem., vol. 15, 1934, p. 413; Chem. Abs., vol. 28, 1934, p. 5806.

Investigation into the optimum conditions for formation of MeOH and CH_2O when working in a closed cycle. The possibility of isolating appreciable quantities of the principal oxidation product of CH_4 (MeOH) by raising the total pressure while at the same time remaining far enough from the limits of inflammability of CH_4–O_2 mixtures, seems to be due only to the selective increase in the rate of the reaction $CH_4+0.5\ O_2=CH_3OH$, relative to all the other reactions possible. This possibility is still further increased, and for the same reason but to a much greater extent, by increasing the ratio of CH_4 pressure to O_2 pressure. Temperature has but a very slight effect on the yields, the optimum detected at 450° being due to the fact that oxidation of MeOH starts long before that of CH_4 and that toward 500° it proceeds at an increasingly rapid rate. Industrial application can be conceived only by utilizing intensive circulation to compensate the low conversion resulting from the necessarily small O_2 content of the mixture.

2568. Paris, A. [Metal Carbonyls.] L'Industrie chimique, vol. 38, May 1951, pp. 125–131.

Reviews preparation, structure, and applications of metal carbonyls. Under applications the promotion of the Oxo reaction by carbonylation, the synthesis of saturated acids from olefins and from olefinic acids from acetylenes (carboxylation), direct synthesis of alcohols from olefins, and direct synthesis of acids from alcohols are mentioned briefly.

2569. Parker, A. Fuel Research Board: Its Objects and Achievements. Jour. Inst. Fuel, vol. 17, 1944, p. 90.

Outline of the work of the Coal Survey and its value to industry and a brief review of several researches that have been carried out at the Fuel Research Station, including the hydrogenation of coal, tar, creosote, etc. and hydrocarbon synthesis by the Fischer-Tropsch process.

2570. ———. Oil and Chemicals From Coal. Inst. Fuel, Wartime Bull., June 1944, pp. 161–163; Gas Jour., vol. 243, 1944, pp. 439, 441, 467–468; Colliery Guard., vol. 168, 1944, pp. 409–412, 445–447; Chem. Abs., vol. 38, 1944, p. 5,060.

Chemical products from carbonization represent 7% of the thermal energy of the coal but are 16% of the total value of the products. Various processes that may be used to increase these % include hydrogenation, low-temperature carbonization, Fischer-Tropsch, and MeOH synthesis. Reviews present uses and demands of various classes of chemical products from coal.

2571. ———. Coal, Science, and the Future. Chem. and Ind., vol. 23, 1945, pp. 234–239.

Paper read before the London Section, Society of the Chemical Industry. Some remarks were made in connection with the competitive prospects of petroleum and coal and products derived from them. The processes of synthesizing gasoline from coal either by catalytic hydrogenation or by way of the formation of H_2 and CO were discussed. Some estimates also were made of the possibilities of underground gasification of coal.

2572. ———. Oil-From-Coal Processes in Germany. Inst. Fuel (London) Bull., June 1947, pp. 128–129; Colliery Guard., vol. 174, 1947, p. 176; Gas World, vol. 126, 1947, p. 191, coking sec. pp. 11–12; Chem. Abs., vol. 41, 1947, p. 5282.

German plants for the hydrogenation of coal reached a capacity of 4,000,000 tons/yr. in 1944, with the greatest recorded production about 3,500,000 tons, a very considerable expansion over the prewar capacity. There was no great expansion in capacity of Fischer-Tropsch plants, which had a combined capacity of 740,000 tons/yr. and actual production of slightly more than 570,000 tons at the maximum. Natural oil resources reached 2,000,000 tons/yr., and 7,000,000 tons were imported from Rumania, etc. The hydrogenation process gives good yields of aviation and motor fuel, while the Fischer-Tropsch process produces some motor fuel of lower quality, high-quality diesel oil, and oils and waxes, which are excellent starting materials for various fats and chemicals. German costs for gasoline were >1 s. per imperial gal., and British costs would be more than 2 times as great; however, the process might be economical in some of the British dominions where lower-cost coal is available.

———. *See* abs. 2602.

Parker, A. M. B. *See* abs. 2119.

2573. Parks, G. S. Thermal Data on Organic Compounds. I. Heat Capacities and Free Energies of Methanol, Ethyl Alcohol, and *n*-Butyl Alcohol. Jour. Am. Chem. Soc., vol. 47, 1925, pp. 338–345; Chem. Abs., vol. 19, 1925, p. 1,085.

Specific heats of crystalline and liquid MeOH, EtOH, and BuOH were measured in an aneroid calorimeter with Cu block as a thermostat from liquid-air temperature to 25°. The accuracy was 0.5%. MeOH has a 2d crystalline form with a transition at 161.1° K. Its heat of transition is 4.4 cal./gm. at 161.1° K. Its specific heat at 168.3° K., 0.40 cal./gm. Its heat of fusion at 175.3° is 23.7.

2574. Parks, G. S., and Hoffman, H. M. Free Energies of Some Organic Compounds. Chemical Catalog Co., New York, 1932, pp. 113–123.

3 methods for developing the free-energy equation for the reaction $CO+2H_2=CH_3OH$ (g) are reviewed: (1) The application of the 3d law of thermodynamics to the available thermal data; (2) direct measurement of the equilibrium constant at 1 or more temperatures; (3) calculation based on measurements of equilibria in the methyl formate reactions. The 1st method is considered the most accurate, and the equation adopted is: $\Delta F^\circ_{298}=-17{,}660+17.5T \ln T-0.0136T^2-57.2T$.

2575. Parravano, N. [Some Economic Aspects of the Synthesis of Alcohols.] Chim. et ind., Special No., April 1934, pp. 125–134; Chem. Abs., vol. 28, 1934, p. 5803.

Address discussing the following phases of the problem: Production of gases for synthesis from water gas or from whole gas with catalystic conversion of CO; production from gas obtained from O_2 generators; production by means of the gasification of lean fuels by O_2; production from natural gas and from petroleum refinery gases; and synthesis from saturated and from unsaturated hydrocarbons.

2576. Parry, V. F., Wagner, E. O., Koth, A. W., and Goodman, J. B. Gasification of Subbituminous Coal and Lignite in Externally Heated Retorts. Ind. Eng. Chem., vol. 40, 1948, pp. 627–641; Chem. Abs., vol. 42, 1948, p. 3929.

During the war the Bureau of Mines conducted experimental work on 2 pilot plants for gasification of low-grade fuels. The experimental data resulting from operation of the externally heated alloy retorts for a total of 3,500 hr. are summarized in graphs and tables, and the fundamental theories of gasification and heat transfer are discussed. The theory of the annular retort and mechanism of gasification therein are presented. It is shown that $CO+H_2$ can be made at rates of 65–70 ft.^{3} per hr. per ft.^{2} of heated surface in retorts heated to 1,900° F. The performance of various processes for production of $CO+H_2$ is compared on the basis of ft.^{3} per hr. per ft.^{2} of fuel-bed area. The Lurgi and Winkler generators, respectively, make 1,000–8,600 ft.^{3} of $CO+H_2$ per ft.^{2}, while externally heated processes make 1,000–2,300 ft.^{3} Various grades of water gas having H_2: CO ratios ranging from 1.9–10 were made in the pilot plants, but it is indicated that lowest-cost gases and highest efficiency and capacity are attained when making gases of 2.0: 2.5 H_2: CO ratio. The performances of 3 externally heated processes, the Didier-Bubiag, the Freiberger, and the annular retort, are reported with operating data. The Didier-Bubiag process was operated in Germany and supplied about 7% of the synthesis gas converted to liquid fuel by the Fischer-Tropsch process. This retort employs refractory chambers and each unit makes about 17,500 ft.^{3} of gas per hr. at an efficiency of about 78%. The 48-in. diameter annular alloy retort at Grand Forks has about the same capacity and has a present indicated efficiency of 71%. Calculations given show that the efficiency of externally heated continuous retorts should be about 80% when equipped with heat-recovery devices. In considering the economics of externally heated retorts, it is shown that the cost of alloy is about $0.01 per 1,000 ft.^{3} of $CO+H_2$, assuming that a 0.25-in.-thick alloy plate will have an average life of 10,000 hr. at 1,900° F. It is therefore indicated that, when making $CO+H_2$ at a rate of 70 cu. ft./hr./sq. ft. in the externally heated retort, the equivalent cost of O_2 to make the same gas in an internally heated process would be $0.03–$0.05 per 1,000 ft.^{3}

2577. Parry, V. F., Gernes, A. C., Wagner, E. O., Goodman, J. B., and Koth, A. W. Gasification of Lignite and Subbituminous Coal, Progress Report, 1945–46. Bureau of Mines Rept. of Investigations 4128, 1947, 68 pp.

Details of the design, construction and operation of 2 pilot plants for gasifying low-rank fuels. The work was part of a program to make reducing gases from lignite for beneficiation of low-grade Fe ores. The results of the work proved that the composition of water gases derived from low-rank fuels could be varied over a wide range. By changing the concentration of steam and the temperature around the retort, water gases having H_2: CO ratios of 2.15: 5.43 were obtained in the larger plant and ratios of 10.0 in the smaller. The indicated overall efficiency of gasification was 72%, when it is assumed that producer gas and steam for the process can be generated at efficiencies of 80–85%, respectively.

2578. Partington, J. R., and Shilling, W. G. Water-Gas Equilibrium. Jour. Soc. Chem. Ind. (London), vol. 44, 1925, pp. 149–150T, 242T; Chaleur et ind., vol. 7, 1926, p. 683; Chem. Abs., vol. 19, 1925, pp. 1769, 2267.

To determine the value of *K* in the equation $([CO_2]\times[H_2])/([CO]\times[H_2O])=K$, the value −0.4647 has been selected for the integration constant in the equation $\log K=-(2226/T)+1.077 \log T-0.0_{3}898T+0.0_{6}133T^2+C$. Values for *K* for each 100° interval from 1,100° abs. to 1,800° abs. are given. The equation and curve presented represent the most reliable data at present available. Previous equations were based on inaccurate specific-heat data.

2579. ———. Calculations on the Water-Gas Equilibrium. Jour. Soc. Chem. Ind. (London), vol. 51, 1932, pp. 82T. 222T; Ind. Eng. Chem., vol. 24, 1932, pp. 591–593; Chem. Abs., vol. 26, 1932, pp. 2575, 3172.

Bryant's criticisms (*see* abs. 396) of their original paper (abs. 2578) are based on a mathematical error in tabulation, which was corrected. Bryant's reply is included.

2580. Pascal, P. [Catalytic Hydrogenation—Synthesis of Methanol.] Tech. moderne, vol. 17, 1925, pp. 449–456; Chem. Abs., vol. 19, 1925, p. 2990.

Review of preparation of H_2, synthesis of MeOH, hardening of fats, hydrogenation of aromatic hydrocarbons, berginization, and cracking.

2581. ———. Fuel Problem. [Coordination of the Three Most Important Synthesis Processes: Fischer Synthesis, Hydrogenation and Methylation.] Tech. moderne, vol. 28, 1936, pp. 393–397; Brennstoff-Chem., vol. 18, 1937, pp. 347–348.

Description of the Fischer-Tropsch synthesis, the Bergius hydrogenation, and the Michot-Dupont methylation processes. It is suggested that a complete coordination of the 3 processes be made, as follows, in order to increase the yields of synthetic gasoline from brown coal and peat: Methylating low-temperature carbonization with fractionation and removal of aromatics; hydrogenation of the heavy liquid residues; gasification and Fischer treatment of the semicoke. This would give maximum yield and quality of gasoline and low capital and operating costs and eliminate coke and byproducts, and at the same time it would supply aromatics for enriching natural products of low octane index. Example: Ordinary low-temperature carbonization of lignite would yield only 19 l. of gasoline b. 250°, whereas low-temperature methylation would give 50 l. per ton; by hydrogenating the heavy-tar residue an estimated 95 l. per ton would be given, and the gasification of the coke residue to synthesis gas and treatment by the Fischer process would increase the yield to a total of about 200 l. per ton of gasoline of an aromatic-aliphatic nature. Michot-Dupont process further discussed in abs. 2582.

2582. ———. [Michot-Dupont Process for Low-Temperature Carbonization of Coal.] Tech. moderne, vol. 28, 1936, pp. 832–839; Teer u. Bitumen, vol. 35, 1937, pp. 38–39.

Ground coal is uniformly moistened with 2% aqueous Ca acetate, mixed with Fe filings and Na_2CO_3 and distilled in a continuous horizontal retort. A tar containing phenols 0.9, aromatic compounds 73, saturated hydrocarbons 18, and unsaturated hydrocarbons 8% is obtained, as compared with a normal tar containing 40.2, 43.0, 11.0, and 5.8%, respectively.

2583. Pascal, P., and Botolesen, E. [Methane Synthesis From Carbon Monoxide and Water Vapor.] Jour. usines gaz, vol. 54, 1930, pp. 467–468; Compt. rend., vol. 191, 1930, pp. 186–187; Chem. Abs., vol. 24, 1930, p. 5282.

When a mixture of CO and H_2O vapor in excess is passed over $NiCO_3$, prepared from $Ni(NO_3)_2$ by precipitation with $MgCO_3$ and forming by heating to 700°, the superposition of 2 limited reactions is observed, the first starting at 250° and yielding CH_4 quantitatively to 275°, above which temperature the second reaction, giving CO_2 and H_2, begins. This reaction is appreciable at 300°, and at 750° the production of CH_4 is completely eliminated. At the higher temperatures the % production of CO and H_2 increases while that of CO_2 and CH_4 diminishes.

2584. Paschke, M. [Gas Production with Use of Oxygen by the Thyssen-Galocsy Process.] Stahl u. Eisen, vol. 60, 1940, pp. 934–935; Chem. Zentralb., 1941, I, p. 602; Chem. Abs., vol. 36, 1942, p. 2705.

Thyssen-Galocsy producer for the production of water gas or synthesis gas from coal or coke by the action of O_2, and steam is diagrammatically described.

Pastonesi, G. *See* abs. 2391, 2392.

2585. Patart, G. [Synthesis of Methanol by the Reduction of Carbon Monoxide.] Compt. rend., vol. 179, 1924, pp. 1330–1332; Chem. Abs., vol. 19, 1925, p. 814.

Mixture of CO and H_2, 1: 2, by vol., was circulated in a closed system for 3 hr. Pure ZnO, granular or suspended on asbestos, was used as a catalyst at 400°–420° and 150–259 atm. In a portion of the system cooled to 20° a liquid composed almost entirely of H_2O and MeOH collected. At the end of the run the volume of CO and H_2 remaining was about 1: 1. Gives complete analyses of the gas mixtures before and after the experiment.

2586. ———. [Industrial Production of Methanol by Catalytic Synthesis Under Pressure.] Bull. soc. encour. ind. nat., vol. 137, 1925, pp. 141–173; Chem. Abs., vol. 19, 1925, p. 2026.

This lecture gives a detailed description of the theory and operation of the catalytic synthesis of MeOH from CO and H_2 and serves as a basis for a paper by Lormand in Industrial and Engineering Chemistry (abs. 2141) descriptive of Patart's process.

2587. ———. [New Field of Catalysis Under High Pressure. Commercial Synthesis of Methanol.] Chim. et ind., vol. 13, 1925, pp. 179–185; Chem. Abs., vol. 19, 1925, p. 1556.

Fuller account is given of the experiments than appeared in Compt. rend., vol. 179, 1924, pp. 1330–1332 (abs. 2585). A small-scale plant erected in 1922 is described. The mixture of water gas and H_2 is compressed to 500 atm., freed from oily impurities in a scrubber, and passed through the catalyst chamber. On leaving this, the MeOH produced is condensed by water cooling and the gases are returned to the process. The condensate is a greenish, turbid liquid, owing to the presence of salts of Zn, Cu, and Fe, the 1st derived from the catalyst and the last 2 from the apparatus, and amounting to 0.5 gm. in 154 cc. The liquid after distillation yields 80% of its original volume of MeOH with traces of acids, higher alcohols, and NH_3 but no acetone or formaldehyde, the remainder being water. Fe, Ni, and Co must be excluded as at temperatures above 300° they catalyze other reactions such as $2\,CO=CO_2+C$ and $CO+3H_2=CH_4+H_2O$. They cannot therefore, be used in the heating elements of the catalyst chamber. No gas purification such as is necessary in the synthesis of NH_3 is required. It is estimated that 100 l. of MeOH can be produced from 300 m.^{3} of water gas at a cost of 25–35 gold francs.

2588. ———. [Commercial Transformation of Coal Into Technical Organic Products.] Chim. et ind., vol. 16, 1926, pp. 713–729; Chem. Abs., vol. 21, 1927, p. 639.

Discussion of the advantages and possibilities of Patart's process for the production of MeOH from CO and H_2 (abs. 2585, 2586, 2587), which also can give higher alcohols under suitable conditions. In using coal as a raw material, most economical and efficient operation is obtained by first distilling for gas and then gasifying with steam to produce water gas, and the process could readily be installed in connection with gas works.

2589. ———. Industrial Transformation of Bituminous Coal into Organic Technical Products. Proc. Internat. Conf. Bituminous Coal, 1926, pp. 132–160; Tech. Eng. News M. I. T., vol. 8, December 1926, pp. 260–262; Fuel, vol. 6, 1927, pp. 160–170; Chem. Abs., vol. 21, 1927, p. 2371.

General discussion of the high-pressure synthesis of alcohols from water gas, including consideration of the effect of inerts in the reaction gas. The cost of production of MeOH under present U. S. conditions is estimated at $0.20 per gal.

———. *See* abs. 122.

Patscheke, G. *See* abs. 3374.

2590. Paul, H. [Economic and Thermal Efficiency of Fischer-Tropsch Synthesis.] Chemie-Ing. Tech., vol. 21, 1949, p. 110; British Abs., 1949, B, I, p. 560.

Thermal efficiency of the synthesis at low pressure is about 44 and that at medium pressure 38–41% corresponding with a consumption of 3.8–4.1 kg. of fuel per kg of product. Reviews range of byproducts.

2591. Paul, H., and Tramm, H. [Fischer-Tropsch Synthesis for Coal Improvement and Power Generation.] Erdöl u. Kohle, vol. 2, 1949, pp. 229–237; Chem. Abs., vol. 43, 1949, p. 7,212.

Emphasizes importance of the Fischer-Tropsch synthesis in German economy. Application of the Ruhrchemie process will make it possible for Fischer-Tropsch plants to contribute greatly to gas supply and to satisfy peak gas requirements for industrial and home consumption. The large production of valuable raw materials for the manufacture of soap, sulfonated alcohols, waxes, etc., is an essential element for German recovery.

2592. Pauling, L. Nature of the Interatomic Forces in Metals. I. Phys. Rev., vol. 54, 1938, pp. 899–904; Chem. Abs., vol. 33, 1939, p. 1205.

It has been generally assumed that in the transition elements (Fe, Co, Ni, Cu) the 3*d* shell is filled with 10 electrons or is nearly filled, and that the *d* electrons make no significant contribution to the cohesive force in metals. Evidence is now presented showing that about half of the *d* orbitals (2.56 of the total of 5) are involved in bond formation, and that the number of covalent bonds resonating among the available interatomic positions increases from 1 to nearly 6 in the sequence K, Ca, Sc, Ti, V, Cr; remains nearly constant from Cr to Ni; and begins to decrease with Cu. The remaining 2.44 *d* orbitals, with very small interatomic overlapping, are occupied by nonbonding electrons, which are mainly responsible for the ferromagnetic and paramagnetic properties of the metals. This point of view provides a qualitative explanation of many properties of the transition metals, such as interatomic distance, characteristic temperature, hardness, compressibility, and coefficient of thermal expansion, and it accounts satisfactorily for the observed values of the atomic saturation magnetic moments of the ferromagnetic elements, Fe, Co, Ni, and their alloys. It also provides a reason for the occurrence of the positive exchange integrals, which give rise to ferromagnetism.

2593. ———. Nature of the Interatomic Forces in Metals. II. Atomic Radii and Interatomic Distances in Metals. Jour. Am. Chem. Soc., vol. 69, 1947, pp. 542–553; Chem. Abs., vol. 41, 1947, p. 5772.

Concept that the metallic bond is equivalent to resonating covalent bonds permits the formation of a system of atomic radii that can be used to calculate interatomic distances in metals and intermetallic compounds and to interpret observed interatomic distances in terms of the electronic structures of the crystals. An equation is developed to express the change in covalent radius (metallic radius) of an atom with change in bond number, or in coordination number, if the valence remains constant; the stabilizing, bond-shortening effect of the resonance of shared-electron-pair bonds among alternative positions also is taken into consideration. This equation is applied to the empirical interatomic-distance data for the elementary metals to obtain a nearly complete set of single-bond radii. Cr, Mn, and Sn exist in metals in 2 forms: A small, high-valent form and a larger, low-valent form. Both kinds of Mn atoms coexist in α– and in β–Mn. In many metals, each atom is attached to some of its neighbors by strong bonds and to others by much weaker bonds. An extreme case is β–W, in which there are straight strings of strongly bonded atoms; similar strings also are present in the α–U structure. The use of the radii is illustrated by application to the *structure of cementite* and *AuSn*.

2594. Pavcek, P. L. Production of Fatty Acids From Byproducts of the Fischer-Tropsch Process. CIOS Rept. XXVIII–35, 1945, 3 pp., PB 4,291; TOM Reel 198.

Paraffins produced by the Fischer-Tropsch process (m. p. 50°–55° and consisting of C_{20}–C_{26} hydrocarbons) are oxidized with air at 130°–150°, using $KMnO_4$ as catalyst in Al towers. Oxidation is not complete and the Mn salts of the fatty acids must be separated from the unreacted paraffin by means of alcohol and C_6H_6. After neutralization with NaOH or Na_2CO_3, the crude soaps are steam-distilled at 250°. The lower fatty acids, such as formic, acetic, propionic, and butyric, come off immediately and the hydroxy acids are converted to unsaturated acids. Keto acids also are removed at this point by the Hader process. The olefinic and saturated acids remaining as the Na salts from the above distillation are set free with HNO_3, and the $NaNO_3$ is removed. The free acids are steam distilled by the Wecker method of forcing water into the hot fat. This method avoids polymerization and keto acid formation and high-grade fatty acids are obtained. The fatty acids are esterified with glycerol (made from propylene) to form soaps or edible triglycerides. Oppau and Witten utilize 20,000 tons/yr. of paraffin, the Märkische Seifenindustrie uses even larger quantities. The overall yield of fatty acids is about 50%. The C_8–H_{10} alcohols obtained as byproducts form excellent plasticizers when esterified with phthalic anhydride (abs. 186).

2595. ———. Research on Synthetic Fats at University of Leipzig. PB Rept. 25,677, 1945, 2 pp.

Report chiefly concerns the research work done by Dr. K. Thomas on the utilization and metabolism of synthetic fatty acids produced by Märkische Seifenfabrik in Witten, Ruhr. Thomas found that these synthetic fats were only partly utilized by the bodies of both humans and dogs.

2596. Pavlyuchenko, M. M. [Fundamental Equation of Topochemical Reactions That Are Not Catalyzed by the Solid Reaction Product.] Jour. Phys. Chem. (U. S. S. R.), vol. 23, 1949, pp. 809–812; Chem. Abs., vol. 43, 1949, p. 8820.

If a reaction that has started on a crystal face is propagated at equal rates along the surface and normal to it, the rate of *v* of reaction is proportional to t^2. If the reaction spreads over the surface more rapidly than it penetrates into the crsytal, *v* is maximum at $t=0$; *t* is time.

2597. ———. [Reactions Involving Solids in the Absence of Any Catalytic Action of the Reaction Products.] Jour. Phys. Chem. (U. S. S. R.), vol. 23, 1949, pp. 800–808; Chem. Abs., vol. 43, 1949, p. 8820.

The corners of a cube are its most reactive points. If the reaction starts from the corners and proceeds along the diagonals of the cube, the area of the reactive surfaces increases; this explains the usual autocatalytic acceleration of reactions involving solids. The theory is applicable also to reactions starting at crystal edges. In both instances, the rate of reaction passes through a maximum.

2598. Pearson, B. M. [Petrol Synthesis From Methane. The Hydrocol Process.] Ann. mines et carburants, Oct. 15, 1946; Gas Times, vol. 50, 1947, pp. 104–105.

Describes process, its development, and advantages. Gives operating principles, describes a commercial test-scale plant, and discusses a project for a large-scale plant.

2599. Pease, R. N. Catalytic Combination of Ethylene and Hydrogen in the Presence of Metallic Copper. I. Measurements of Reaction Velocity and Adsorption Isotherms at 0° and 20°. Jour. Am. Chem. Soc., vol. 45, 1923, pp. 1196–1210; Chem. Abs., vol. 17, 1923, p. 2220.

Kinetics of the catalytic combination of H_2 and C_2H_4 have been studied at 0° and 20° in the presence of Cu. The reaction velocity and adsorption isotherms have been determined. Within limits, the velocity increases with the H_2 concentration but decreases as the C_2H_4 concentration increases. The temperature coefficient of the reaction velocity/10° rise between 0° and 20° is 1.62, indicating that diffusion does not play a dominant part.

2600. Pease, R. N., and Chesebro, P. R. Equilibrium in the Reaction $CH_4+2H_2O \rightleftharpoons CO_2+4H_2$. Jour. Am. Chem. Soc., vol. 50, 1928, pp. 1464–1469; Chem. Abs., vol. 22, 1928, p. 2139.

Reaction $CH_4+2H_2O \rightleftharpoons CO_2+4H_2$ has been studied at 500° and atmospheric pressure. Equilibrium was approached from both sides and the value of the constant found to be 0.037 (partial pressures being expressed in atmospheres) at 505°. This is in excellent agreement with the value calculated from Lewis and Randall's free-energy equations and thus supports in particular their equation for CH_4 in the low temperature region. It is pointed out that the reactions $CH_4+H_2O \rightleftharpoons CO+3H_2$ and $CO_2+H_2 \rightleftharpoons CO+H_2O$ also are to be taken into account at higher temperatures. Equilibrium constants at 500°, 600°, and 700° are given for reference. Attention is called to the CH_4–steam reactions as a source of H_2 and of H_2–CO mixtures.

2601. Pease, R. N., and Stewart, L. Catalytic Activity and Adsorptive Power of Supported Iron, Cobalt, Nickel, Copper, and Silver. Jour. Am. Chem. Soc., vol. 49, 1927, pp. 2783–2787; Chem. Abs., vol. 22, 1928, p. 345.

Samples from a uniform supply of diatomite brick were impregnated with solutions of the nitrates of Fe, Co, Ni, Cu, and Ag, in the proportions of 1 gm.-atom of metal per 100 gm. of dry brick, in order to insure that the differences in catalytic activity of the supported catalysts thus prepared might be due only to the specific properties of the metal in question. The apparatus, the static method of measuring the catalytic activity of these catalysts for the hydrogenation of C_2H_4, and the method of measuring the adsorption of H_2 and C_2H_4 were the same as previously described in abs. 2599. Co and Ni caused instantaneous hydrogenation of C_2H_4 at −20°; Fe was moderately active at 0°, Cu at 50°, and Ag at 100°. Much more H_2 was adsorbed by Ni and Co than by the other metals, and more C_2H_4 by Fe. Reaction velocity measurements with Ag at 100° and Cu show that the rate is proportional to the H_2, and independent of the C_2H_4 concentration. With Fe at 0°, excess H_2 increases the rate, while excess C_2H_4 has little effect. An association, rather than a dissociation theory of catalytic hydrogenation, is indicated.

2602. Peck, E. B., and Parker, A. Production of Synthesis Gas From Powdered Brown Coal or Coke at H. Koppers G. m. b. H., Essen. CIOS Rept. XXVIII–36, 1945, 4 pp., PB 417; TOM Reel 198; British Abs., 1946, B, I, p. 159.

Cost estimates for the production of 10^5 m.^{3} of synthesis gas per hr. Flow sheets for (*a*) the conversion of coke-oven gas into synthesis gas, and (*b*) low-temperature carbonization, followed by gasification of bituminous coal.

Peebles, W. C. *See* abs. 1440, 1441, 1442, 1443, 1444, 1445, 1446, 1447, 1448, 1449, 1449a.

Pepper, W. P. *See* abs. 141.

Perkins, P. D. *See* abs. 6.

2603. Pernoux, E. [Examination Under the Electron Microscope of Some Kieselguhrs Utilized as Catalyst Supports.] Compt. rend., vol. 228, 1949, pp. 1,646–1,647; Chem. Abs., vol. 43, 1949, p. 8,831.

About 50 samples of 4 different commercial kieselguhrs were examined under the electronic microscope: A crude Filter-Cel, an acid-treated Filter-Cel, an acid-treated Filter-Cel followed by treatment with 5% Na_2CO_3, and a crude Filter-Cel treated with 5% Na_2CO_3. A magnification of 6,000 was adopted. The micrographs are described but not illustrated. Taking account of the fact that the kieselguhrs are made up of 95% of hydrated amorphous silica to which are added some silicates and various impurities (Al_2O_3 and Fe oxide), the following interpretations can be made. The acid treatment of the crude product causes the superficial formation of a silica gel, which seals the pores. This silica is redissolved by treatment with 5% Na_2CO_3. The direct carbonate treatment of the initial product involves only a small part of the silica consisting of the most finely divided portions. The microscopic examination thus confirms the conclusions made by Teichner.

2604. ———. [Use of the Electron Microscope in the Study of Catalyst Supports.] Jour. chim. phys., vol. 47, 1950, p. 233; Chem. Abs., vol. 44, 1950, p. 7635.

Treatment of kieselguhr with HNO_3 and HCl caused the formation of a SiO_2 gel. The gel was completely removed by reaction with 5% Na_2CO_3. Alkali treatment of raw kieselguhr dissolved only the smallest particles. The results confirmed the conclusions drawn by Teichner (abs. 3362).

———. *See* abs. 3363, 3363a.

2605. Perrault, R. [Synthetic Production of Motor Fuels According to the Fischer Process.] Rev. indust., vol. 65, 1935, pp. 373–376; Chem. Zentralb., 1936, I, p. 2011; Chem. Abs., vol. 31, 1937, p. 5973.

Summarizes discussion of benzine synthesis by the method of Fischer and Tropsch.

2606. ———. [Some New Uses of Cobalt.] Génie civil, vol. 108, 1936, pp. 254–257; Chem. Abs., vol. 30, 1936, p. 7516.

Stellite and the newer alloys of Co with Be, Ti, and Al are mentioned. Some of the hard Co alloys in the form of frit are mixed with powdered diamond. Co is used as a catalyzer in the Fischer process for synthetic production of light oils, also for plating.

2607. Perrin, M. [Evolution of Activity of Fischer-Tropsch Catalysts.] Compt. rend., vol. 224, 1947, pp. 342–343; Chem. Abs., vol. 41, 1947, p. 3739.

Fischer and Meyer (abs. 988) observed that CO was completely hydrogenated to CH_4 in the presence of a fresh catalyst. Craxford (abs. 637) attributed the hydrogenation to metallic Co, and the synthesis of higher hydrocarbons to Co carbide. Earlier it was observed that where the CO and H_2 were diluted with CH_4, condensable hydrocarbons were formed at once. Now it has been found that N_2 produces the same effect, and, in general, lowering the partial pressure of CO and H_2 inhibits the formation of CH_4 almost completely. Lowering of the synthesis temperature from 190° to 175°, as well as a reduction in the flow of the reactants, also reduces the necessary delay in the starting of the synthesis reaction. These observations indicate that the initial production of CH_4 is due to overheating the catalyst bed and that any method of preventing this temperature rise starts the hydrocarbon synthesis without the formation of excessive CH_4.

2608. ———. [Chemical Evolution of Fischer Catalysts During the Thermal Reducing Treatment.] Compt. rend., vol. 227, No. 8, 1948, pp. 476–478; Bull. soc. chim., 1949, No. 5–6, pp. 366–367; Chem. Abs., vol. 43, 1949, p. 26.

Ni catalysts on kieselguhr with small amounts of ThO_2 or Al_2O_3 were subjected to reducing tests in order to ascertain, as a function of time and temperature, the loss in weight and the amounts of H_2O and CO_2 set free. The catalyst, after drying, tested 26.3% of Ni, the transformation of which to the metallic state involved a loss of 7.2%. A rapid heating up to 450° in a stream of H_2 for 127 min. caused a loss in weight of 24.8%, and in N_2, 24%. The same catalyst calcined in air at 900° lost 26.4% of its weight. The brief treatment up to 450° had an almost identical result and was enough to eliminate almost the whole amount of CO_2 and H_2O in the basic carbonates and the other hydrated substances that made up the dried catalyst. With a slower treatment of gradual heating up to 450° during a period of 4 hr., the loss in weight was 28.5%. There was an increased reduction of the NiO. The H_2O and CO_2 set free measured, respectively, 21.4 and 4.85% of the initial weight, the deficit of 2.25% being CH_4, which was carried away in the stream of H_2. At the end of a series of operations at different temperatures and times, the weight of the catalyst had diminished 32.5–32.8%, a result very close to that obtained by calcination in air at 900°, including the total reduction of the NiO (26.4%+7.2%=33.6%). These empirical results, however, do not necessarily agree with general practice; many factors may modify the results. The rate of temperature increase, the length of treatment, and the flow of H_2 affect the various chemical reactions involved such as dehydration, decarbonation, reduction of CO_2 to CH_4, and reduction of NiO. The same parameters must likewise influence the formation of hydrated combinations between the silica of the kieselguhr, the Al_2O_3, and the oxides of the heavy metals, as these combinations are formed very easily under the conditions of preparation and reduction of Fischer catalysts.

2609. ———. [Loss in Weight of a Fischer Nickel Catalyst During Reduction.] Bull. soc. chim., 1949, No. 5–6, pp. 366–367.

Fischer Ni catalysts were heated to 450° in streams of N_2 and H_2; the losses in weight were virtually the same. A very slow reaction was observed at 220°, probably corresponding to a structural change in the catalyst. For a total loss of 28.5% of the initial weight of the catalyst, 21.4% was represented by H_2O and 4.85% by CO_2. The deficit of 2.25% was logically attributed to a slow reduction of CO_2 into CH_4, which dissolved in the H_2 and thereby was not measurable. In reducing the catalyst by successive steps of temperature maintained until the weight of the catalyst became constant, it was found that at 120° the loss in weight was rapid and virtually complete in 2 hr.; at 210° the loss was rapid at the beginning and then slow for about 50 hr.; at 360° the loss occurred in about 5 hr. and likewise at 450°. The losses were respectively, 9.4, 12.6, 9.1, and 1.7.

2610. ———. [Thermal-Reduction Treatment of Fischer Catalysts.] Jour. chim. phys., vol. 47, 1950, pp. 262–268; Chem. Abs., vol. 44, 1950, p. 7638.

Catalyst containing 26.3% Ni, small amounts of Mn, and Al with kieselguhr as support was studied. The total loss in weight and the amounts of H_2O and CO_2 formed were determined during successive reductions at 120°, 225°, 360°, and 450°. The total loss in weight was 32.5% and consisted of H_2O, 26.36; CO_2, 3.24; and presumable CH_4, 2.90%. All of the CO_2 evolved was formed at or below 225°.

———. *See* abs. 779, 2743, 2744, 3229, 3426, 3427, 3428.

2611. Perruche, L. [Synthetic Foods.] La Nature, No. 3146, 1947, p. 327.

Brief review of the manufacture of synthetic fats from Fischer-Tropsch paraffin.

2612. Perry, C. W. German Chemical Engineering. A Survey 1935–45. Chem. Eng. Progress, vol. 43, No. 12; Trans. Am. Inst. Chem. Eng., 1947, pp. 659–666.

2613. Perry, C. W. Evolution of the Petrochemical Industry. Oil Gas Jour., vol. 48, No. 21, 1949, pp. 66, 67, 82, 84, 87, 88.

Comprehensive summary of the petrochemical industry is presented, and the important sources of petroleum chemicals are reviewed. The possibilities in the production of oxygenated chemical byproducts of the Fischer-Tropsch synthesis are discussed.

2614. Perry, G. T. Fuels and Lubricants From Sources Other Than Petroleum. Canadian Chem. Process Ind., vol. 32, 1948, pp. 624–629.

Review of the production of fuels and lubricants by the hydrogenation of coal and by synthesis from natural and water gas. It is concluded that Canada can be made independent of outside sources of crude-oil supplies by utilizing coal resources lying within its geographical boundaries, using either the Hydrocol or the Synthine process.

Perry, H. *See* abs. 810a.

2615. Perry, H., Corey, R. C., and Elliott, M. A. Continuous Gasification of Pulverized Coal With Oxygen and Steam by the Vortex Principle. Trans. Am. Soc. Mech. Eng., vol. 72, No. 5, 1950, pp. 599–610; Chem. Abs., vol. 44, 1950, p. 7510.

This report presents the preliminary results of a Bureau of Mines investigation of the gasification of pulverized coal by steam–O_2 mixtures in a vortex reactor. The theory of the vortex is explained, the basic principles of reactor design is set forth, and an illustrative example of their application is given. A method of calculating the composition of the gas produced in this reactor is advanced and has been checked experimentally. The C conversion and the limits of operation have been found to be closely related to the type and uniformity of the coal distribution. A method of improving the operation of the equipment and the quality of the gas by a change in the type of coal distributor from the conical to the spinning-plate form appears to offer considerable advantages.

Perry, L. R. *See* abs. 1105.

Persson, O. *See* abs. 1385.

2616. Pertierra, J. M. Errors in the Determination of Gas Temperatures With Thermocouples. Ion, vol. 10, 1950, pp. 395–401; Chem. Abs., vol. 45, 1951, p. 1861.

Discrepancies in gas temperature measurement with thermocouples and methods for elimination of the errors due to radiation are reviewed.

———. *See* abs. 419.

2617. Petch, N. J. Positions of the Carbon Atoms in Austenite. Jour. Iron Steel Inst. (London), vol. 145, 1942, pp. 111P–128P; Chem. Abs., vol. 36, 1942, p. 6477.

X-ray powder photographs of austenite show that the possible positions for C are at the centers of the unit cells and at the midpoints of the edges. Discusses theories of the structure.

2618. ———. Interpretation of the Crystal Structure of Cementite. Jour. Iron Steel Inst. (London), vol. 149, 1944, pp. 143P–150P; Chem. Abs., vol. 38, 1944, p. 4891.

Cementite is essentially a framework of close-packed Fe atoms with the small C atoms in the largest interstices held in place by metallic bonding. The lattice parameters of cementite have a small but systematic and definite decrease with increasing quenching temperature. Variation in the Fe : C ratio is the explanation of the lattice parameter variation. The most possible variation in composition is by omission of C atoms to a limited extent. 9 refs.

———. *See* abs. 2120.

2619. Peters, —. [Treatment of Kogasin.] TOM Reel 170, frames 415–419, July 18, 1939.

Catalytic cracking is superior to thermal cracking under pressure. Since cracking catalysts polymerize easily, they should be used first for polymerization and then for cracking. Si–Al as well as H_3PO_4 catalysts were being considered.

2620. Peters, K. [Progress in the Improving and Utilizing of Coal.] Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 552–568.

General survey, including the benzine synthesis from coal and water gas.

———. *See* abs. 994, 995, 996, 997, 1034, 1035.

2620a. Peters, K., and Kappelmacher, E. Conversion of Hydrocarbons to Carbon Monoxide–Hydrogen Mixtures. Brenstoff-Chem., vol. 33, 1952, pp. 296–307; Chem. Abs., vol. 47, 1953, p. 290.

Thermodynamic calculations were made for CH_4 splitting with air, steam and CO_2 over the entire temperature range of practical interest and the exact theoretical cracked-gas composition determined corresponding to the practically important CO–H_2 mixtures. Ni catalysts were prepared with which these reactions were studied on a laboratory scale, with good agreement between theoretical and experimental results. Catalytic splitting of CH_4 is more rapid with air or O than with CO_2 and steam. The experiments gave some light as to the reaction mechanism and assisted in minimizing soot formation. Soot formation can be reduced by lowering the partial pressure of the hydrocarbons by adding an excess of steam, dilution with inert gases, or by the use of a catalyst of higher activity and selectivity. The results are presented in tabular form and in graphs so the theoretical conditions can be determined for any desired cracked gas composition. Since the thermodynamic final state is dependent only on the temperature and the atomic relation C : H : O : N in the reactants, these results are applicable to all cracking of solid liquid and gaseous fuels with air, O_2, steam and CO_2 as gasification media.

2621. Peters, K., and Küster, H. [Water-Gas Equilibrium Under the Influence of Electric Discharges at Diminished Pressure.] Ztschr. physik. Chem., vol. 148, 1930, A, pp. 284–303; Brennstoff-Chem., vol. 11, 1930, pp. 171–172; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 279–299; Chem. Abs., vol. 24, 1930, p. 4708.

Mixtures of CO and H_2 reacted during electrical discharge at diminished pressure according to the equation $CO_2+H_2=H_2O+CO-10.4$ cal. The yield increased with current density. No marked displacement of the equilibrium was noted between 20 and 60 mm. Hg. The yield remained constant up to a rate of flow of 710 l. per hr. The average temperature in the discharge tube was 300°, while that of the discharge stream was about 800°–1,000°. For mixtures rich in CO_2 the calculated equilibrium temperatures were up to 1,000° higher than the temperatures of the discharge stream, indicating pronounced electrical effects.

2622. Peters, K., and Meyer, K. [Thermal Formation of Acetylene From Methane.] Brennstoff-Chem., vol. 10, 1929, pp. 324–329; Chem. Abs., vol. 24, 1930, p. 484.

Possible reactions are: (1) $2CH_4 \rightarrow C_2H_2+3H_2-91$ cal.; (2) $2CH_4 \rightarrow 2C+4H_2-41$ cal.; (3) $2CH_4 \rightarrow 1/3\,(C_6H_6)+3H_2-42$ cal. Reaction (1) is favored by high temperature and low pressure. Reaction (2) can be suppressed by short heating time. The apparatus consisted of a glass globe with 3 tubulures, 2 of which, being coincident with the globe diameter, served to admit the gas and electric current for heating a W spiral in the center of the globe. Reaction gases were drawn off by the 3d tubulure. With a heating zone 20 mm. long (3 mm. wire) at 3,000° and CH_4 at 50 mm. pressure passed at the rate of 30 l. per hr., 66.5% of the CH_4 was converted into C_2H_2, no C_6H_6 being formed. The heating time was 0.0001 sec. These were the most favorable conditions found for reaction (1).

2623. Peters, K., and Pranschke, A. [Decomposition of Methane With Carbon Dioxide and Water Vapor in the Electric Discharge.] Brennstoff-Chem., vol. 11, 1930, pp. 473–476; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 271–279; Chem. Abs., vol. 25, 1931, p. 645.

At 5,000–6,000 v. in the discharge tube previously described and with rates of gas-flow to 800 l. per hr., CH_4–H_2O and CH_4–CO_2 mixtures have been almost completely decomposed to CO and O_2. Separation of C did not occur, but at intermediate voltages a large part of the CH_4 formed C_2H_2. Tabulated data show that by varying the proportions of the mixture used, variations over a wide limit are possible in the resulting gas. Curves show the relationships between current density, CH_4 content, and the production of CO and C_2H_2.

2624. Peters, K., and Winzer, K. [Cracking of Kogasin.] Brennstoff-Chem., vol. 17, 1936, pp. 429–430; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 503–505.

Cracking of Kogasin II upon graphite is compared with that upon Pt (abs. 1035); the yields are similar.

2625. ———. [Preparation of Light Naphtha From Kogasin II by Cracking.] Brenstoff-Chem., vol. 17, 1936, pp. 301–306; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 506–516; Coal Carbonisation, vol. 2, 1936, p. 205; Chem. Abs., vol. 31, 1937, p. 1992.

Cracking at 465°–570° and pressures to 100 atm. has been studied at throughputs up to 150 cc. oil/min. Cracking was assisted by H_3PO_4 catalyst. The proportion of gaseous to liquid products varied between 1 : 2 and 1 : 6 up to 530° and at 560° attained 1 : 1, as compared with cracking at atmospheric pressure in a Pythagoras tube up to 740° where proportions ranged 2 : 1–6 : 1. Pressure cracking yielded unsaturated compounds in smaller amount, the naphtha obtained, however, being highly unsaturated. Treatment with C_2H_4 in the presence of H_3PO_4 catalyst did not improve the octane number, although C_2H_4 did.

2626. Petersen, W. [Effect of Phenol Content of Flotation Agents in Treatment of Coal Fines.] Bergbau Arch., vol. 8, 1948, pp. 88–103; British Abs., November 1948, B, I, p. 580.

Tar-oil fractions for flotation should contain 4–5% of phenols to promote frothing. Part of the phenols can be supplied by addition of limited amounts of ammoniacal spent liquor containing about 1.8 gm. of phenols/l. Still greater economy of tar oil can be achieved by addition of pine oil. Paraffin is inferior to tar oils unless improved by frothing agents. A synthetic Fischer-Tropsch oil fraction containing no phenols, but 0.7% of saponifiable constituents, when tested in progressively increasing amounts, was comparable initially with tar oils, but its efficiency was not maintained at higher concentrations.

2627. Peterson, S. F. Utilizing Natural Gas Would Aid United States Oil Supply. Oil Weekly, vol. 113, No. 9, 1944, pp. 22, 32; Petrol. Refiner, vol. 23, 1944, p. 145.

It is suggested that the Government could develop application of Fischer-Tropsch process to make synthetic oil from natural gas, thus increasing the liquid-fuel supply and conserving domestic petroleum reserves, rather than giving so much attention to foreign oil fields.

2628. Petroleum (London). Synthetic Fuels in Germany. I. Introduction. Vol. 9, 1946, pp. 74, 93.

Before the war the trend in fuel synthesis was toward the Fischer-Tropsch process, but during the war the Bergius hydrogenation process gained interest. Of the total oil production of 6,180,000 tons in 1943 from all sources, 3,088,000 tons was from Bergius hydrogenation and only 368,000 tons was produced by the Fischer-Tropsch process. Also, attention had been paid to increasing production rather than developing new processes during the war. No evidence has been found of developments that would make either of the processes more attractive economically. The use of pressures above atmospheric and the use of Fe catalysts and processes working in several stages had been investigated in connection with the Fischer-Tropsch process, but extensive plant application has not been established. As regards the use of pressure, drawings were obtained of vessels designed to operate at 10 atm. pressure. The principal feature is the methods used to dissipate the exothermic heat of reaction. Some useful information was obtained regarding operation in stages and recycling. Of particular interest is the Oxo process. Of importance, too, in the production of aviation fuel is the Dehydrierung-Hoch-Druck process, which catalytically dehydrogenates naphthenes to aromatics at 50 atm. and 500°. In this way, the yield of aromatized gasoline is said to be 65% of the feed.

2629. ———. Synthetic Fuels in Germany. II. Hydrogenation. Vol. 9, 1946, pp. 102, 109.

General review of 15 German hydrogenation plants with an annual production capacity of 3,700,000 tons of finished product. Tabulated summary.

2630. ———. Synthetic Fuels in Germany. III. Fischer-Tropsch Process, Lubricating Oils and Acetylene. Vol. 9, 1946, p. 158.

Brief review of the products from the Fischer-Tropsch synthesis, with a description of the Carrieres-Kuhlmann plant at Harnes, France (abs. 1262 and 3038) and of the Oxo process of the Ruhrchemie at Holten (abs. 1363, 1478, and 2177).

2631. ———. Synthetic Fuels in Germany. III (2). Fischer-Tropsch Process, Lubricating Oils and Acetylene. Vol. 9, 1946, p. 191.

2 processes are described briefly: That of the Kuhlmann Co. at Lestaque. France (capacity 25 tons per day) and a pilot plant at Harnes, France. To produce 1 ton of lubricant, the 1st process requires 600 kg Fischer-Tropsch gas oil, 600 of benzol, and 160 of dichlorethane. The gas oil is chlorinated at 90°–100° and is mixed with a benzol-dichlorethane mixture in the presence of $AlCl_3$ at 70° and then raised to 110°. The mixing time is 6 hr.; 10% of $AlCl_3$ is used. The liquid product is stripped of the uncombined benzol, allowed to settle, the $AlCl_3$ sludge is removed by water washing, and the washed oil is blended with gas oil to lower its viscosity and is used as a general machine-lubricating oil where a high-grade oil is unnecessary. The upper layer, after decantation, is clay-treated and distilled, the overhead product (20%) is sent back for reprocessing, the upper side stream product (30%) being used as a transformer oil. The bottoms make a high-grade steam-cylinder oil (20%), which can be used at superheat temperatures up to 350°; 30% of turbine oil also is obtained. The oils formed consist of polybenzenes with long paraffinic chains attached: this structure gives the oils a high viscosity index and a low pour point. The properties of some of the oils are shown in a table. In the 2d process the raw material is Fischer-Tropsch gasoline of as high olefin content as possible. This is mixed with 3% of $AlCl_3$ and remains in contact with it for 5 hr. at room temperature. On standing, 2 layers separate, the lower contains a heavy polymer bound chemically with the $AlCl_3$. It is treated with NaOH and washed with H_2O, leaving a lubricating oil. The upper layer contains paraffinic gasoline and free polymer, the former being removed by steam stripping, the remaining oil is clay-treated and filtered and a gas oil, a light lubricating oil for cold service, and a heavy lubricating oil suitable for ordinary lubrication is prepared. The latter can be hydrogenated at 100 atm. and 200° over the normal Fischer-Tropsch catalyst to produce a substance similar to vaseline. The above oils suffer from poor oiliness and ready oxidation. Properties of 4 oils are given in a table. The article concludes with a description of underground lubricating-oil plants.

2632. ———. Synthetic Plan for India. Vol. 13, 1950, p. 121.

Synthetic petroleum plant, expected to begin production in 1951, is to be built at Orissa, on the east coast of India. The project, prepared by experts of the National Petroleum Institute of Paris, is sponsored by an Indian industrialist, B. Patniak. It is anticipated that the cost of production of petrol will be below the present market price of petrol from crude oil.

2633. PETROLEUM ENGINEER. Synthetic Fuels Made From Dry Gas. Vol. 18, No. 2, 1946, p. 64.

A 10-bbl. per day experimental synthetic oil pilot plant is operating on natural gas at the Baton Rouge plant of the Standard Oil of New Jersey. The technique was developed before and after the war, was used to produce 100-octane aviation gasoline during the war and is now being tested in the production of fuel for automotive equipment of all kinds. These synthetic fuels are now being made from natural gas, but the process is applicable to coal as well and when perfected can serve to extend liquid fuel supplies indefinitely.

2634. ———. New Sulfur-Recovery Process. Vol. 23, No. 2, 1951, pp. C44, C47.

Girdler S-recovery process from H_2S gases is based on a modification of the original Claus process. Reaction is carried out in 2 stages:

$$(1)\ H_2S+3/2O_2\rightarrow SO_2+H_2O;$$

$$(2)\ 2H_2S+SO_2\rightarrow 3S+2H_2O.$$

The process is described by aid of a flow diagram. Up to 95% of the S in H_2S-carrying gas may be recovered. If used in combination with a Girbotol gas purification plant, the utility requirements of the S-recovery plant are minor.

2635. PETROLEUM PRESS SERVICE. Economics of the Fischer-Tropsch Process. Vol. 4, 1937, pp. 448–450.

2636. ———. German Developments. Vol. 5, 1938, pp. 301–304.

It is reported that at the end of 1937 Germany had 4 Fischer-Tropsch plants with a total capacity of 250,000 tons per yr.

2637. ———. Progress in Germany. Vol. 5, 1938, pp. 61–64.

As far as light motor fuel is concerned, the progress made, although falling short of earlier predictions, is estimated to be rapid enough to ensure virtual independence of imports within the next year or two. As regards heavier oils, which represent over ½ of the total requirements, there appears to be no prospect of self-sufficiency being attained in the near future.

2638. ———. New German Plants. Vol. 6, 1939, p. 529.

Plant of Krupp-Treibstoffwerk G. m. b. H. at Essen, which obtains its raw material from coal by low-temperature carbonization by the Krupp-Lurgi process, commenced production of primary product at the end of 1938, and a plant at Deschowitz has been recently completed for the Gräflich Schaffgottsche Benzin G. m. b. H. of the Silesian coal industry.

2639. ———. Soviet Germany—Oil-From-Coal Plans. Vol. 17, 1950, pp. 235–236; Fuel Abs., vol. 8, No. 6, 1950, abs. 4608.

Production of synthetic fuels in the Soviet zone of Germany is planned to reach 840,000 metric tons in 1950, and to rise to 1,260,000 tons in 1955 under a new 5-year plan. Based on lignite, this production meets the zone's requirements of automotive fuels, and has provided small quantities for export to Western Germany. All main plants have passed to U. S. S. R. ownership. Eastern Germany is the only part of Europe where there are fewer commercial motor vehicles than in 1938.

2640. PETROLEUM PROCESSING. Government Research on Synthine Process. Vol. 2, 1947, p. 172.

Some comments are made on the recent report to Congress by the Secretary of the Interior on the Synthetic Liquid Fuels Act. There is little question, it is stated, that the Bureau's work constitutes one of the largest present research programs in the field of synthetic liquid fuels, and that there is little doubt that the program will yield important data, especially if extended at least in time. Proper cooperation with industry and avoidance of unnecessary duplicative work could make this program an outstanding example of Government research in applied fields of science.

2641. ———. Is $30,000,000 More Needed for the Liquid Fuels Program? Vol. 2, July 1947, p. 560.

Editorial criticisms of the Bureau of Mines program. No fault is found with the purpose back of the research program, which is to secure data on methods of producing liquid fuels synthetically, including processes, equipment, and costs, but rather with the manner in which the program is being carried out. It is thought that the Bureau has been far too wasteful and extravagant in its expenditures; too much money has gone for permanent-type laboratories, plants, and offices built to last a lifetime instead of for the length of the program. It also is said that the Bureau attempts to operate on too large a scale; equally reliable cost and operating data for the purpose of the present program could be obtained from laboratory and pilot-plant studies without the expense of installing large demonstration plants. Furthermore, the Bureau too often entirely ignores the advice of its petroleum-industry advisory committee and does not cooperate in a program that would correlate with the established research programs of the oil companies. Some method of obtaining closer control and assuring coordination with the needs of industry should be set up. The solution, perhaps, is an advisory board composed of representatives of industry, the Armed Services, and the Bureau and empowered to actually direct the course of the program. Commenting in Petroleum Processing (vol. 2, July 1947, p. 558) Eugene Ayres, Gulf Research & Development Co., and a member of the Industry Advisory Committee, says that such criticism comes from misunderstanding of the way in which the work is conducted, and that the program of the Bureau has satisfied the specification as set forth by the Advisory Committee.

2642. ———. Oil-Company Synthetic Fuels and Lubes Show Good Records in Navy Tests. Vol. 2, No. 1, 1947, pp. 37–39, 42–44.

Included among the fuels recently tested by the U. S. Navy at Annapolis in actual performance in gasoline and high-speed diesel automotive engines, were the following synthetic fuels and lubricants: The Texas Co.—gasoline and diesel fuel made from natural gas by the Hydrocol process; synthetic lubricating oil prepared by blending a highly refined mineral oil with an ester type synthetic oil of low viscosity. The Union Oil Co. of California—gasoline made from Colorado shale and diesel oil manufactured from shale oil. Standard Oil Development Co.—gasoline and diesel fuel made from natural gas in the modified Fischer-Tropsch unit at Baton Rouge employing the fluid catalyst technique. The Carbide & Carbon Chemicals Corp.—synthetic lubricating oil synthesized from natural gas or other hydrocarbon gases similar to a Society Automotive Engineers 30 grade. The chemical nature or method of manufacture is not yet disclosed. The gasoline and diesel engines powered and lubricated by synthetic products were put through performance tests described by the Navy as highly satisfactory. Liquid fuels made from coal by the Fischer-Tropsch process gave true similarity of performance in the experimental gas turbine to Navy-specification diesel fuel under optimum operating conditions. In gasoline engines the 80-octane synthetic fuel was equal to or better than normal petroleum gasoline. Further studies are to be made in the laboratory and in actual service. Properties of each of the gasolines, diesel fuels, and lubricating oils are tabulated.

2643. ———. Shall Government Permanently Engage in Liquid Fuels Research? Vol. 2, 1947, p. 160.

This editorial criticizes the Bureau of Mines for attempting to extend the synthetic liquid fuels program beyond its originally specified term of 5 yr. Government funds should not be spent on research that duplicates that being carried on by the oil companies, and that the latter are better equipped to do than the Bureau. Government research in connection with the development of liquid fuels should be confined to the assay and analysis of the low-grade coal deposits and the oil-shale beds for their potential value as source material for synthetic fuels when needed some time in the distant future. The use of either of these raw materials in the commercial production of substitute fuels will call for excavating, conveying, and handling solid materials, and, in the case of shale, disposal of solid wastes, on a huge scale. Studies of methods to be applied here and the economics involved are beyond the scope of research and development work of any individual oil company. At present such work is only a small part of the Bureau of Mines program, but it could be expanded and emphasized. It would correlate but not duplicate the studies of actual processing techniques, which some of the oil companies have been engaged in for several years.

2644. ———. Cancellation of Stanolind's Synthine Plant. Vol. 3, No. 10, 1948, p. 926.

Announcement was recently made by the Stanolind Co. that plans for the erection of a synthine plant at Garden City, Kans., were being canceled because of rising costs of construction and difficulty in obtaining materials. From the viewpoint of the petroleum industry, this occurrence may have unfortunate repercussions in that it weakens the industry's recent arguments that it can stand on its own feet in regard to building synthetic fuels plants and that there was no need for Government entry into competition with private industry in setting up a synthetic fuels industry. If the economics on which the Stanolind decision was based are universally applicable, it would appear that the petroleum industry is in no financial position to construct a large-scale synthetic fuels industry in the immediate future. The need for such an industry at the present time is somewhat debatable, but it is highly likely that sooner or later it will actually be needed for national security; the decision to erect one should not be left to Government forces with possible eventual Government control of the entire petroleum industry. Although this cancellation is a small matter commercially, it should not be seized upon as a sign of petroleum-industry weakness, which it certainly is not.

2645. ———. Gas-Synthesis Plant. Vol. 5, No. 9, 1950, pp. 946–947.

Major construction work has been completed on the Bureau of Mines gas-synthesis demonstration plant at Louisiana, Mo., which will convert coal into liquid fuels by a modified Fischer-Tropsch process. The plant, of 80–100-bbl. per day capacity, was built at a cost of $4,915,000. It is expected to begin integrated operations early next year. Modifications of the German Fischer-Tropsch process include improvements in the method of producing and purifying the synthesis gas, the use of a rugged, granular, synthetic-NH_3 type Fe catalyst, and the use of a fluidized-bed, internally cooled converter. The synthesis gas will be obtained by gasifying pulverized coal ranging from anthracite to lignite with O_2 and superheated steam. O_2 for the process will be extracted from the air at temperatures of more than 300° F. below zero in a Linde-Fränkl unit; it will be 98% pure. The gasification unit is briefly described. It will use about 28 tons of coal, 24 of O_2, and 35 of superheated steam to produce 2,000,000 ft.^{3} of raw synthesis gas daily. It is already demonstrated that a gas of normal composition (41% CO, 38% H_2, 16% CO_2, and 5% N_2 and impurities) can be produced. As an auxiliary source of synthesis gas, a 7-ft.-diameter Kerpely producer modified to operate continuously with coke and O_2 has been installed. Anticipated daily production will be 55–60 bbl. of 75-octane gasoline, 10–12 bbl. of 80-octane diesel oil, and about 12 bbl. of heavy oils and waxes suitable for cracking stock. Process-flow diagram of the plant is shown.

2646. Petroleum Refiner. Hydrocol Process. Vol. 26, No. 4, 1947, p. 240. Process Handbook Section.

Description, with flowsheet of the Hydrocol process as licensed by the Texaco Development Corp.

2647. ———. Need for Synthetic Fuels. Vol. 27, No. 3, 1948, pp. 141, 143.

Summary of the current possibilities and developments in Government participation in the synthetic fuels program.

2647a. ———. Lukuga Synthetics Plant Possibility for Congo. Vol. 31, No. 8, 1952, p. 62.

Possibility of establishing a synthetic oil plant in the Belgian Congo by the Lukuga Coal Syndicate has already passed the study stage. Several hundred ton of coal have been shipped from the Lukuga Basin to Belgium for testing to determine its adaptability for transformation into gas and to choose the most appropriate method of gasification. The syndicate was organized in 1950 to study the possibility of establishing a synthetic fuels plant in the Belgian Congo. The Congo has coal deposits but no known oil resources.

2648. Petroleum Times. New Synthetic Oil Processes in Germany. Vol. 48, 1944, p. 28.

Reference to recent work described by Dr. F. Fischer. Mention of new raw materials for manufacturing synthesis gas and of work with new and more effective catalysts. Increasing the octane number of synthetic oils has received attention. The synthesis of carbohydrates as found in nature is visualized.

2649. ———. Chemical Derivatives of Coal and Home Refining of Petroleum. Vol. 49, 1945, p. 1078.

Excerpts from a report of a nonparty technical committee of 4 fuel technologists to draw up a policy for fuel utilization. Encouragement should be given to the extension of the chemical utilization of raw materials derived from coal. In the United States a synthetic organic chemical industry is being developed, which has no parallel in England, and the latter country has clearly lagged behind other nations in its researches on chemicals derived from petroleum and coal. It is urged that a Fischer-Tropsch plant should be erected for intensive study on the same lines as the coal-hydrogenation plant erected by the Imperial Chemical Institute. The British Coal Utilization and Research Association is starting work on chemical utilization problems, and its work should be encouraged.

2650. ———. Synthetic Motor-Fuel Production. Vol. 51, 1947, pp. 613 and 614.

Synthetic motor fuel is now being produced in the Soviet zone of Germany at the monthly rate of 80,000 tons, or nearly as much as was obtained during the early part of the war from the synthetic gasoline plants now under Russian control. These consist mainly of the Leuna and Brabag Works. The machinery for the Oswiecim plant being brought to Poland as German reparations is being assembled. When the plant goes on stream at the end of 1948, its output should be about 20,000 tons of synthetic gasoline per yr. The Peat Institute of Russia has worked out a scheme for the complete utilization of peat burned in power stations. The process consists in treating the peat chemically by means of gasification before sending it to the power station. The power station receives excellent gaseous fuel, and what remains of the peat after the treatment is used to make synthetic gasoline. The process of complete utilization of peat reduces capital expenditure on synthetic gasoline production by 20%, cost of the product by 18%, and peat consumption in power stations by 30–35%.

2651. ———. Oil Production in South Africa. Vol. 52, 1948, p. 989; Ind. Chem., vol. 24, 1948, p. 715.

In Government Gazette, October 9, 1948, announcement was made of license issued to Anglo Transvaal Consolidated Investment Co., Ltd., for manufacture of liquid fuels and oils from coal. The plant is to have an approximate capacity of 76,000,000 gal. of liquid fuel and oil per yr. It will operate a process for catalytic conversion of synthetic gases from carbon-bearing material into petroleumlike hydrocarbons. Production is to begin within 4 yr. The authorized capital of the company will not exceed £13,000,000.

2652. ———. Synthetic Alcohol by New "Esso" Process. Vol. 53, No. 1342, Jan. 14, 1949, p. 43.

Commercial production of iso-octyl alcohol has been announced by Esso Standard Oil Co. The process involves reaction of a selected gasoline fraction with H_2 and CO at pressures up to 3,000 p. s. i. Although iso-octyl, as such, has possibilities as a resin solvent and antifoaming agent, its principal value is as intermediate or raw material for other chemicals. It can be converted to wetting agents, or to metallic salts that make effective paint driers.

2653. Petrov, A. D. [Formation of Petroleum of the Naphthene Type. Transformation of Aliphatic Acids Into Hydrocarbons Under High Pressure.] Jour. Russian Phys.-Chem. Soc., vol. 61, 1929, pp. 1849–1859; Ber. deut. chem. Gesell., vol. 63B, 1930, pp. 75–84; British Chem. Abs., 1930, A, p. 322; Chem. Abs., vol. 24, 1930, p. 2696.

By cracking lactic acid in the presence of lime and H_2O, an oil was obtained identical with that obtained by the hydrolysis of cellulose and differing from Fischer's Synthol chiefly in containing less alcohol. Treatment with H_2SO_4 gave hydrocarbons identical with the corresponding Synthin fractions. Fischer and Schrader have found that lactic acid is the chief product in the hydrolysis of cellulose.

2654. ———. [Synthesis of Motor Fuel From Carbon Monoxide and Hydrogen.] Jour. Appl. Chem. (U. S. S. R.), vol. 5, 1932, pp. 274–284; Chem. Abs., vol. 26, 1932, p. 4932.

Review.

2655. ———. [Synthetic Liquid Fuel and Its Importance for the Ural-Kuznetzkii Basin.] Acad. Sci. Petrograd, 1932, 143 pp.; Chem. Abs., vol. 27, 1933, p. 1135.

Discussion of coal liquefaction, low-temperature carbonization and cracking of low-temperature carbonization tar, synthesis of hydrocarbons from CO and H_2, condensation of olefins from coke-oven plants and cracked gases, cracking of CH_4, condensation of C_2H_2, hydrogenation of naphthalene and other components present in tars, synthetic liquid fuel by fermentation and its byproducts, combined synthetic hydrocarbon and fermentation plants, properties of mixtures containing benzene, gasoline, and alcohol as motor fuels, and automobiles with gas producers using charcoal.

2656. ———. [Gases Obtained in Low- and High-Temperature Carbonization as Raw Material for Commercial Organic Synthesis.] Khim. Tverdogo Topliva, vol. 6, 1935, pp. 82–92; Chem. Abs., vol. 29, 1935, p. 7616.

Review with 28 refs.

2657. ———. [Synthesis of Gasoline From Gases.] Khim. Tverdogo Topliva, vol. 8, 1937, pp. 981–996; Uspekhi Khim., vol. 6, 1937, pp. 1509–1525; Chem. Zentralb., 1938, II, p. 631; Chem. Abs., vol. 32, 1938, p. 5187.

Comprehensive review, with 65 refs.

2658. Petrov, A. D., and Vittikh, M. V. [Synthesis and Properties of Isoparaffinic Hydrocarbons of the Composition C_{17}–C_{24}.] Bull. acad. sci. U. R. S. S., Classe sci. chim. 1944, English summary, pp. 238–242; Chem. Abs., vol. 39, 1945, p. 1618.

Pr hexyl ketone was treated with $CH_2:CHCH_2MgCl$ to yield hexylpropylallylcarbinol, b_7 116°–118°, d_{20}^{20} 0.8482, n_D^{15} 1.4535: dehydration over Al_2O_3 gave a mixture of 4–propyl–1,3–decadiene and 4–propyl–1,4–decadiene, b_6 85°–88°; hydrogenation over Pt black gave 4-propyldecane, b. 214.5°–215.5°, d_{20}^{20} 0.7716, n_D^{20} 1.4354. Dihexyl ketone treated with BuMgBr gave 7–butyl–7–tridecanol, b_{10} 163°–165°, d_{20}^{20} 0.8350, n_D^{20} 1.4489, which was dehydrated by boiling with I to yield an isomeric hydrocarbon mixture, b_9 140°–147°; hydrogenation of the latter over Ni oxide at 240°–250° gave 7-butyltridecane, b_{12} 147°–148°, d_{20}^{20} 0.7793, n_D^{20} 1.4355. Crude methyldioctylcarbinol (admixed with some olefin) was prepared from EtOAc and C_8H_{17} MgBr; this was dehydrated by boiling with I to yield 9-methylheptadecene, boiling at 169°–174° (no pressure given), d_4^{20} 0.7916, n_D^{20} 1.4472, freezing point 26.5°; hydrogenation of the latter over Ni gave 9-methylheptadecane. b_{10} 172°–174°, d_4^{20} 0.7810, n_D^{20} 1.4388. C_8H_{17} MgBr and dihexyl ketone gave 7–hexyl–7–pentadecanol, b_7 196°–197°, d_{20}^{20} 0.8420, n_D^{20} 1.4519; dehydration with I gave an isomer mixture b_7 181.5°–183°; hydrogenation of the mixture over Ni oxide at 220°–250° gave 7–hexylpentadecane, $b_{9.5}$ 182°–183°, d_{20}^{20} 0.7923, n_D^{20} 1.4419. Et caprylate and C_8H_{17} MgBr gave a mixture of 9–heptyl–9–heptadecanol and its dehydration product (pure alcohol b_9 230°–231°, d_{20}^{20} 0.8470, n_D^{20} 1.4538); after the usual dehydration the olefin mixture b_9 206°–212° was hydrogenated over Ni at 250° to yield 9–heptylheptadecane, b_8 210°, d_{20}^{20} 0.8009, n_D^{20} 1.4465. The C_{17}, C_{21}, and C_{24} compounds have cetane numbers near 100 and have satisfactorily low melting points in the continued study of compounds having good antidetonating properties.

Petrova, L. V. *See* abs. 804.

Petrova, N. Y. *See* abs. 279, 281, 282.

2659. Petty, M. Scanning Washington's Oil Horizon. Petrol. Eng., vol. 18, No. 12, 1947, p. 14.

Military leaders apparently have become convinced that development of a synthetic fuel industry in the United States, capable of producing 1,000,000 bbl. per day of synthetic oil, is the only sure way of attaining the self-sufficiency required by national defense. As the result of recent conferences between officials of the Interior Department and of the Army and Navy, a plant-construction program, costing several hundred million dollars, may be submitted at the next session of Congress. The program probably will call for building 4 synthetic plants, each with a capacity of 25,000–30,000 bbl. per day to make liquid fuels by retorting oil shale, by hydrogenation of coal, and by the Fischer-Tropsch process using natural gas and coal. Preliminary to this, the Bureau of Mines, at the request of the military, has launched an immediate survey for suitable locations for synthetic plants with a capacity of 1,000,000 bbl. per day. As an indication of the task ahead in making the Nation self-sustaining in synthetic liquid-fuel resources in the face of a natural petroleum shortage in the not too distant future, it was recently pointed out by W. G. Greenman, Director of Naval Petroleum Reserves, that to provide 1,500,000 bbl. of synthetic fuel per day (500,000 bbl. from each of shale, coal, and gas, using the Fischer-Tropsch process for the latter two cases), the following would be needed: total plants, 65 (15 for shale, 25 for each of coal and gas); steel, 9,500,000 tons; construction costs, $4,300,000; mine costs, $650,000,000; and staff for plant operations and mining, 148,000 men. It is estimated by the Bureau of Mines that synthetic plants smaller than those contemplated by the military would be nearly competitive with petroleum refineries; for a 10,000-bbl. per day plant producing motor fuel from bituminous coal at $1.50 per ton the net cost would be 8.7 cents per gal. while a 20,000-bbl. shale oil plant could make synthetic crude oil for $1.92 per bbl., exclusive of profit and interest on the investment.

2660. Peusel, —. Lubricants and Surface Protection in the Metal Industry. TOM Reel 53, February 1945, frames 62–95.

Discusses some important developments in the field of lubricants. The starting material is Kogasin, obtained as a product of the Fischer-Tropsch synthesis and hydrogenated into Mepasin. It was found that a derivative of this, Mepasin sulfonamido acetic acid, had outstanding qualities as a lubricant in metal working, both for cutting, drilling, and milling and for hot and cold shaping, deep drawing of wire, etc. The product is used as an emulsion, both because the lubricating effect is not affected and savings are made, and because this greatly reduced the danger of plant fires. There is presented during the discussion what appears to be a relatively new theory of film formation, lubricating effect, and adhesion to metal. The theory involves molecular polarity, formation of supermolecular structures in the nature of liquid colloidal crystals, the interplay of surface forces, and other novel hypotheses that appear to be solidly grounded and highly illuminating. It is claimed that the new Mepasin derivatives actually make pretreatment of metal blanks in deep-drawing operations unnecessary.

2661. Pew, J. E., and Dotterweich, F. H. Maximum Hydrocarbon Utilization With Natural Gas as a Chemical Raw Material. Petrol. Refiner, vol. 23, No. 4, 1944. pp. 130–134; Gas, vol. 20, No. 4, 1944, pp. 14–16, 19–20; Chem. Abs., vol. 38, 1944, p. 2475.

Known natural-gas reserves are estimated to be sufficient for at least 30 yr. and large quantities of natural gas are still being wasted. The liquid constituents of natural gas now serve as a source for chemicals, including aviation gasoline and solvents. Expansion is possible in this respect. Dry natural gas can be used for many purposes; it can readily be re-formed to water gas, and about 50% of the emergency synthetic NH_3 is made with H_2 from this source. The Fischer-Tropsch process can produce liquid hydrocarbons from this re-formed natural gas, but it is probable that this process will only be operated at remote points where pipelines are not available. It is estimated that 4.2 gal. of liquid products are recoverable from 1,000 ft.³ of dry natural gas.

2662. ———. Science in Natural Gas. Gas Age, vol. 949, 1944, pp. 19–21, 62, 64, 66. Petrol. Refiner, vol. 23, December 1944, pp. 92–96; Nat. Petrol. News, vol. 37, No. 1, 1945, pp. R–11, 12, 14, 79; Am. Gas Assoc. Monthly, vol. 27, 1945, pp. 103–106, 148.

Combination of the Fischer-Tropsch process and the natural gas-steam reaction to produce liquid hydrocarbon fractions on a favorable economic basis could result in an enormous amount of natural gas being used, thereby depleting our natural-gas reserves. The operation of pilot plants indicates a favorable economic conversion with plans for at least 1 commercial plant underway.

Pflegling, —. *See* abs. 2878.

2663. Philippovich, A. [Decomposition of CO With and Without Catalysts.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 37–43.

Review of literature.

Phillips, J. R. *See* abs. 576.

2664. Phillipson, G. A. Coke-Oven Managers Association Presidential Address. Gas World, vol. 125, No. 3248, supp., 1946, pp. 10–14.

It is proposed to make use of central coal-carbonizing plants interconnected by gas grids and then installing synthesis plants operating on both gas and coke, whichever should be in excess supply at any time, thereby increasing the benefits derived from full-capacity operation of the carbonizing plants.

Phinney, J. A. *See* abs. 2834, 2835.

2665. Phragmen, G. [Stability of Cementite and the Various Forms of Carbon.] Jernkontorets Ann., vol. 114, 1930, pp. 431–442; Chem. Abs., vol. 25, 1931, p. 271.

Critical review of the literature. Conclusion: The evidence indicates that cementite becomes stable at higher temperatures.

———. *See* abs. 3669.

2666. Pichler, H. [Coal as a Source of Raw Materials.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 734–737; Chem. Abs., vol. 26, 1932, p. 3899.

2667. ———. [Progress in the Field of Coal Utilization.] Ztschr. Ver. deut. Ing., vol. 74, 1930, pp. 720–722; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 594–604; Chem. Abs., vol. 24, 1930, p. 3879.

Discusses chemical improvement of coal, especially from the viewpoint of producing liquid fuel.

2668. ———. [Effect of Pressure on the Conversion of Water Gas.] Brennstoff-Chem., vol. 12, 1931, p. 235.

Paper presented at the meeting of the Verein Deutscher Chemiker in Vienna, May 1931. Increased pressure hinders the gasification of carbonaceous substances with steam, owing to the masking of the surface by inert gases. If this inactivity is prevented by means of increased temperature or by the addition of alkali, a secondary formation of hydrocarbons occurs through the action of the nascent H_2 on the C present. Increased pressure in the catalytic hydrogenation of CO favors the deposit of high-molecular products on the catalyst. Thus the catalyst activity deteriorates much fasten than at 1 atm. pressure. At higher pressures acid-containing products take the place of the hydrocarbons. Diminished pressure is unfavorable for the formation of hydrocarbons since for the same amount of conversion larger amounts of catalyst are necessary. The nature and the speed of CH_4 cracking with CO_2 or steam is strongly influenced by pressure. At 1/100 atm. and 500°–600° all of the CH_4 is converted into CO and H_2, whereas at atmospheric pressure a temperature of 900°–1,000° is required. The speed of reaction increases in proportion to the diminution in pressure.

2669. ———. [Influence of Pressure on Several Conversions of Water Gas.] Ztschr. angew. Chem., vol. 44, 1931, p. 472.

Paper presented before the Fachgruppe für Brennstoff and Mineralölchemie in May 1931.

2670. ———. [Synthesis of Gasoline at 200° C. and Atmospheric Pressure.] Ztschr. Ver. deut. Ing., vol. 79, 1935, pp. 883–885; Coal Carbonisation, vol. 1, 1935, pp. 101–103.

In the Fischer-Tropsch process, Fe, Co, and Ni are found to be the best catalysts for the conversion of $CO–H_2$ into hydrocarbons. Their action probably involves the temporary formation of carbides. However, to obtain the best results, it has been found necessary to employ combinations with other metals in specific amounts. Thus far the best yields have been obtained with a Co–Th–Cu–kieselguhr catalyst precipitated with soda under defined conditions. This yielded 105–110 and even over 120 gm. of liquid hydrocarbons per $m.^3$ of gases in a single pass, and maintained 80% of this yield after 60 days, during which period the catalyst-absorbed up to 150% of its weight of hard paraffin. After appropriate regeneration the catalyst can be used again. The synthesis proceeds at about 200° C. and atmospheric pressure; about 75% of the original gas is converted. Complete conversion results in the liberation of about 600 kgcal. per $m.^3$ of gas or about 20% of the heat of combustion, therefore, the removal of the heat is an important problem and is solved by circulation of oil through the contact chamber and a steam generator for utilization of the heat extracted. The mixture of gases for the synthesis of gasoline consists of CO and H_2 in the ratio of 1:2. If unsaturates are desired in the products, a higher proportion of CO is used. The S content of the synthesis gas should not exceed 0.2 gm. per 100 cu.m. The products of synthesis from a $29:58=CO:H_2$ mixture with Co catalyst, in weight %, consisted of gasol, 4% (boiling below 30°); gasoline or Kogasin I, 62% (boiling at 30°–200°); oil or Kogasin II (boiling above 200°); solid paraffin from oil, 7% (m. p. 50°); hard paraffin from catalyst, 4% (m. p. 70°–80° or more). The gasoline is low in antiknock properties; the octane No. of the 30°–180° C. Kogasin fraction is 67 with 0.5 cc. of $PbEt_4$ per l. and 71.5 with 1 cc. per l. The Kogasin II is an excellent diesel fuel. The synthetic paraffin is of specially high purity. An increased yield of gasoline can be obtained by subjecting the higher boiling Kogasin II to cracking by the usual methods of petroleum technology. The unsaturated hydrocarbons in the synthesis products can be varied by altering the composition of the initial gas and the catalyst; they are important as the raw materials for the manufacture of pure higher alcohols or esters. For the manufacture of lubricating oils (1) the fractions containing olefins are treated with 5% by weight of $AlCl_3$, (2) the high-boiling fractions low in olefins are chlorinated and then converted to Cl-free viscous oil by activated Al_2O_3, (3) chlorinated Kogasin with aromatic hydrocarbons is condensed in presence of $AlCl_3$. Such lubricants combine a favorable viscosity index with a low setting point (—42° C. compared with —16° C.) for a commercial winter oil.

2671. ———. [Working Up Fischer-Tropsch Products.] Brennstoff-Chem., vol. 16, 1935, pp. 404–406; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 481–486; Chem. Abs., vol. 30, 1936, p. 3980.

Synthetic-paraffin oil boiling at over 250° has been converted at 500°–600° and atmospheric pressure without carrier gas, in one step, into gaseous olefins and volatile unsaturated and aromatic hydrocarbons with 75% yields. The remainder consisted of saturated gaseous hydrocarbons, unconverted paraffins, and aromatic tar. Below 500°, conversion was small. Above 600°, yields of gaseous olefins predominated. Example: 20% olefins at 550° and 0.4 sec. reaction time in small tubes, 60% at 700° and 0.14 sec.

2672. ———. [Discovery and Synthesis of New Paraffins of Very High Molecular Weight.] Brennstoff-Chem., vol. 19, 1938, pp. 226–230; Petrol. Ztschr., vol. 34, No. 38, 1938, pp. 1–5; Chem. Abs., vol. 33, 1939, p. 120.

In preliminary pressure hydrogenations with noble-metal catalysts, mixtures of $1:2$ $CO:H^2$ heated to 140° in contact with reduced Ru oxide at 150 atm., while paraffins accumulate upon the catalyst. These are completely soluble only in boiling ether, C_6H_6, or toluene and are separated with boiling toluene or xylene into fractions, the highest m. 120°–132°. Repeated hydrogenation is made with 3 gm. catalyst in a heated-steel tube with continuous flow of the gas mixture exhausted at 1 l./hr. and starting at 15 atm. and 140°, the temperature is increased 10° each 24 hr. Conversion begins at 160°, with 7% contraction in gas volume at 180°, increasing to 24% at 240°. The solid and liquid reaction products, melting clear at 111°, are recovered in maximum yield at over 70% contraction at optimum conditions of 200° and 100 atm. At 50–100 atm., over 90% of the O_2 in the CO forms H_2O; only below 50 atm. and above 200° are appreciable amounts of CO_2 formed. Small amounts of fatty acids are formed with the reaction H_2O. No decrease in catalyst activity is observed in 26 wk. of continuous use. The oil-free solid paraffins constitute 60–70% of the product by the butanone method and m. 118°–119°. Of these, 13% are insoluble in boiling C_6H_6 and m. 126°–128°. The 53% soluble in boiling C_6H_6, m. 113°. Subsequent extraction of the Ru catalyst with boiling toluene yields a paraffin m. 132°. All the paraffins recovered, recrystallized, and washed with MeOH and distilled ether have the composition C_nH_{2n+2}. Determination of molecular weight by boiling point elevation, mostly in toluene, show a range of 2,100–8,000, or 170–670 C atoms, for the 5 paraffins m. 123.5°–131.5° extracted from the catalyst. These are situated upon the upper extension of the hyperbolic C atom: melting point curve of *n*–paraffins. The 1:1 addition of kieselguhr to the Ru is without effect. At atmospheric pressure, Pt produces no solid or liquid products, whereas Os and the remaining noble metals, beginning at 215°, produce small amounts of gaseous hydrocarbons other than CH_4 becoming inactive at 315° to produce only CH_4. Under pressure, considerable yields are obtained with Rh and Os, the first giving contractions similar to Ru but with O-containing compounds, the latter reaching an activity at 220° to produce gaseous hydrocarbons. Pt is even less active while only traces of hydrocarbons are obtained with Pd and Ir.

2673. ———. Lecture and Discussion on Iron Catalysts for the Middle-Pressure Synthesis, Sept. 9, 1940. TOM Reel 101; Transl. on TOM Reel 244, 21 pp.

In general, it has been found that the best catalysts are those prepared by precipitation of ferric nitrate solutions with Na_2CO_3 or NH_3; they are designated normal Fe catalysts. They must be inducted before use, and the best method, therefore, appears to be that of passing pure CO at lower pressures and higher temperatures than are used in the following synthesis and at a high gas velocity, for example: 1/10 atm., 255°–325°, and 400 l. of CO gas/kg. Fe/hr. The induction period is terminated when the formation of CO_2 has passed through a maximum and has reached a more or less constant minimum value, generally in about 25 hr. With a catalyst thus inducted, a synthesis pressure of 15 atm., a temperature of 235°, and a synthesis gas composition of $3\ CO:2\ H_2$, maximum yields of 130–160 gm./N $m.^3$ of gas can be obtained. An Fe catalyst made and operated as above had a life of 1½ yr. without regeneration at a temperature of 260°; it still gave a yield of 140 gm./N $m.^3$ The ideal synthesis gas was produced by passing CO_2 and steam over hot coke according to the equation $5\ C+4\ H_2O+CO_2=6\ CO+4\ H_2$. The CO_2 for the conversion is obtained by scrubbing the end gases from the synthesis process. Addition of small amounts of alkali (0.5–5% K_2CO_3) to the Fe catalyst has no important effect on the total yield of products but does change their quality, an increase in the paraffins and oxygenated products and a decrease in the liquid and gasol hydrocarbons with increasing alkali contents. The lifetime of the catalyst also is longer at a low alkali content (1% K_2CO_3 or other alkaline salt) than it is at a higher content. It was found that treatment of the catalyst with H_2 either before induction with CO or between the induction period and the synthesis proper offers no improvement in the activity of the catalyst. Some increase in the activity and a better stability of the catalyst does, however, result by interrupting the synthesis and treating with H_2; this must be done before the catalyst has deteriorated to a great extent. The use of kieselguhr as carrier in the Fe catalyst is detrimental to its activity unless added after alkalization. As regards mechanism of the induction process, it is assumed that the primary reaction is the reduction of the ferric oxide into ferromagnetic Fe_3O_4, which, at the low temperature and pressure of the induction, is converted directly into carbide by action of the CO without going through the FeO phase. In presence of 100% CO induction gas and at the low pressures and high CO velocities used during the induction, the CO_2 is rapidly removed from the catalyst and the carbide remains stable without oxidation. The action of CO on the Fe catalyst is 3-fold: the reduction process differs from the H_2 reduction, the CO deposits free C on the catalyst thus loosening the crystal lattice and making more surface available for the reaction, and carbides are formed. With a $CO+H_2$ mixture, liquid and solid hydrocarbons are forming on the catalyst surface and preventing the activating gases from coming in contact with the catalyst. Some description is given of the products of the middle-pressure synthesis. The Fe catalysts are not only superior to the Co catalysts because of their cheapness, but also for the cheaper apparatus required and the more stable lifetime that they exhibit. The antiknock properties of the benzine made with the Fe catalyst are better than those made with the Co catalyst, and the unsaturated gasol hydrocarbons can be used to greater advantage for production of high-quality benzine. Fe catalysts have the disadvantage of working at higher temperatures, hence greater steam pressure, if cooling is done with H_2O. Furthermore, they have a greater tendency to form C than do the Co catalysts. This report includes the only published data on induction methods for Fe catalysts. The documents translated are: PG–21559–NID; PG–21574–NID (lecture by Dr. Pichler); PG–21581–NID (recent investigations); and PG–21577–NID (behavior of Fe catalysts where operated with H_2-rich synthesis gas.)

2674. ———. [Town Gas in Conjunction With Kogasin Synthesis.] Brennstoff-Chem., vol. 22, 1941, pp. 244–248; British Chem. Abs., 1942, I, p. 218B; Chem. Abs., vol. 36, 1942, p. 6329.

Possibility of obtaining town's gas of specified properties, for example, calorific value 4,200–4,600 kcal./$m.^3$, d. 0.4–0.5, and Ott number 60–100, by mixing residual gas from the Fischer-Tropsch hydrocarbon synthesis process with water gas in suitable proportions, converting CO into H_2 and CO_2, and removing CO_2, is discussed theoretically. The effects on the composition of the town gas obtained of changing the $CO:H_2$ ratio of the synthesis gas, the type of synthesis catalyst employed, and the presence of CO_2, N_2, and CH_4 in the synthesis gas are illustrated by examples.

2675. ———. [Formation and Decomposition of Formic Acid and Formates.] Brennstoff-Chem., vol. 24, 1943, pp. 27–31; Chem. Abs., vol. 37, 1943, p. 6644.

Review with over 50 refs., most of which are incorporated in this bibliography. From experiments conducted by the author, it is found that under suitable conditions of pressure, temperature and catalysts, it is possible to synthesize a relatively high % of free HCOOH from CO and H_2O or CO_2 and H_2. The production of sugar is a possibility.

2676. ———. [Reaction of Carbon Dioxide During Hydrogenation.] Brennstoff-Chem., vol. 24, 1943, pp. 39–40; Chem. Zentralb., 1943, I, p. 2556; British Chem. Abs., 1944, B, p. 194; Chem. Abs., vol. 37, 1943, p. 6526.

In the Fischer-Tropsch synthesis, CO_2 does not react in the presence of CO; atomic H is assumed to be necessary for the hydrogenation of CO_2. Only little chemisorbed H_2 is present on the catalyst surface during the formation of higher hydrocarbons. The hydrogenation of CO_2 does not follow the same course as that of CO. HCOOH may be considered the first intermediate product in the hydrogenation of CO_2 and it is converted isomerically into dioxymethylene. The next stage is CHOH with liberation of H_2O from which

CH_4 or MeOH is formed according to the reaction conditions.

2677. ———. Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Bureau of Mines Special Rept., June 1947, 159 pp.

Comprehensive review of the development of the Fischer-Tropsch hydrocarbon synthesis at the Kaiser Wilhelm Institut für Kohlenforschung, and of the most-important work connected therewith. Consideration is given to the historical background; the normal pressure synthesis, its catalysts, and products; medium-pressure synthesis with Co and Fe catalysts and its products; modifications of these processes, such as hot gas recycle, liquid-phase catalyst suspension process, oil recycle; high-pressure synthesis of paraffin with Ru catalysts; isosynthesis in presence of oxide catalysts (ThO_2); and mechanism of the hydrogenation process.

2678. ———. [Development of Gasoline Synthesis in the United States. Hydrocol Process.] Brennstoff-Chem., vol. 30, 1949, pp. 105–109; Chem. Abs., vol. 43, 1949, p. 7664.

Development of the Fischer-Tropsch process in the United States is reviewed. Stress is laid on the use of a fluidized catalyst (alkalized Fe) and the use of a highly efficient external heat exchanger to remove the heat of reaction; this avoids the use of numerous small internally cooled catalyst chambers as in Germany. This catalyst is poisoned by S but is not affected by the formation of small amounts of C, although excessive amounts of C reduce its efficiency. The gasoline consists of a mixture of primary gasoline and polymerization gasoline. The C_3–C_4 fraction is nearly 100% saturated. The gasoline has an octane number of about 80 motor method. Brief reference is made to costs, and a simplified flow sheet is given.

2678a. ———. Fischer-Tropsch and Related Processes for Synthesis of Hydrocarbons by Hydrogenation of Carbon Monoxide. Advances in Catalysis, Academic Press, Inc., New York, 1952, vol. 4, pp. 271–341.

2678b. ———. [Review of 25 Years Research on the Fischer-Tropsch Synthesis and Related Processes With Especial Attention to the Reaction Mechanism Involved.] Brennstoff-Chem., vol. 33, 1952, pp. 289–296; Chem. Abs., vol. 47, 1953, p. 290.

Review, with 44 refs.

———. *See* abs. 872, 999, 1000, 1001, 1002, 1003, 1004, 1005, 1006, 1007, 1008, 1009, 1010, 1011, 1036, 1037, 1038, 1039, 1040, 1041, 1048, 1837.

2679. Pichler, H., and Buffleb, H. [Behavior of Ruthenium Catalysts in Synthesis of Paraffin Hydrocarbons of High Molecular Weight.] Brennstoff-Chem., vol. 21, 1940, pp. 273–280; Chem. Zentralb., 1941, I, p. 1118; Chem. Abs., vol. 36, 1942, p. 2253.

Activity of the catalyst was the same whether it was first reduced with H_2 or with $2H_2+CO$ at atmospheric pressure, or was reduced directly with synthesis gas under pressure without pretreatment. The normal gas rate used was 5 l. per hr. with 3 gm. of Ru; with falling gas rate, the conversion into liquid and solid hydrocarbons rose to approximately the theoretical value. The yield per hr. reached a maximum (300–350 gm. per l. of catalyst space) at a gas rate of 10 l. per hr. per gm. of Ru. Data on the variation of the yield with temperature and pressure are tabulated. Yields remained approximately constant over 200 days' operation at 195° per 100 atm., and thereafter slowly diminished; after 560 days, when the temperature had been raised to 215°, the yield was 140 gm. per m.³, that is, only 10% less than the initial value. Addition of alkali (K_2CO_3) to the catalyst had little influence on its activity or on the ratio of liquid to solid hydrocarbons in the product. Addition of H_3PO_4 or phosphates did not improve the catalyst. By carrying out the synthesis with a Ru catalyst suspended in H_2O at 150°, a high proportion of paraffins of high melting point, insoluble in boiling C_6H_6, was obtained. Briefly discusses the mechanism of the reaction.

2680. ———. [Properties of Some Solid Paraffins Produced From Carbon Monoxide and Hydrogen at High Pressures on Ruthenium Catalysts, With Special Reference to the Previously Unknown Highest Melting Constituents.] Brennstoff-Chem., vol. 21, 1940, pp. 285–288; Chem. Zentralb., 1941, I, p. 119; Chem. Abs., vol. 35, 1941, p. 7365.

Paraffins were fractionated by means of solvents and the ultimate analysis, mean molecular weight, melting range, density, and viscosity of each fraction were determined. The dependence of melting point and viscosity on molecular weight is shown graphically. The highest melting fraction (132°–134°) had a mean molecular weight of 23,000 and d^{20} 0.980. A comparison of paraffins formed on the Ru catalysts with those from medium pressure synthesis on Co catalysts showed that the former have the higher melting range. The production of such paraffins has not been possible so far by any other process.

2681. ———. [Synthesis of Paraffin Wax on Ruthenium Catalysts at Pressures up to 1,000 Atmospheres.] Brennstoff-Chem., vol. 21, 1940, pp. 257–264; Chem. Zentralb., 1941, I, p. 850; Chem. Abs., vol. 36, 1942, p. 2253.

Gas mixture ($CO+2H_2$) was passed over the catalyst (3 gm. of Ru) at a rate corresponding with 1 l. (normal temperature and pressure) of resultant gas per hr. At 140° the conversion of CO into hydrocarbons rose from nil at 15 atm. to 18% at 100 atm. and 54% at 1,000 atm. (36% of liquid and solid hydrocarbons); at 180° the conversion rose from 11% at 15 atm. to 70% at 100 atm. and 91% at 1,000 atm. (72% of liquid and solid hydrocarbons). At 100 atm. about 65% and at 1,000 atm. about 75% of the liquid and solid hydrocarbons consisted of paraffin waxes of melting point up to 134°. At 200° per 100 atm. and half the above rate of gas passage, yields of 190 gm. per m.³ (normal temperature and pressure) of initial gas, that is, 91% of theory, were obtained. The yields of liquid and solid hydrocarbons varied only slightly with temperature over the range 190°–240°; at higher temperature, especially above 300°, the formation of CH_4+CO_2 became marked. Mixtures of CO_2 and H_2 interacted over a Ru catalyst at lower temperature than $CO+2H_2$ but only CH_4 and H_2O were formed. The presence of CO_2 did not affect the interaction of CO and H_2.

2682. ———. [Synthesis of Free Formic Acid From Carbon Monoxide and Water.] Brennstoff-Chem., vol. 23, 1942, pp. 73–77; Chem. Age, vol. 53, 1945, pp. 463–468; Chem. Abs., vol. 36, 1942, p. 4474.

Formation of formic acid through the direct action of CO and H_2O under pressures up to 2,000 was investigated. At each temperature, a definite state of equilibrium exists between the concentration of liquid formic acid and CO pressures. Certain mineral acids and salts (Cu_2SO_4, $CuCl_2$) and especially H_2S and H_3PO_4 are suited as catalysts. The salts under the conditions of the reaction are reduced to the mineral acids. The optimum conditions for formic acid synthesis are determined.

2683. Pichler, H., and Merkel, H. Chemical and Thermomagnetic Studies on Iron Catalysts for the Snythesis of Hydrocarbons. Bureau of Mines Tech. Paper 718, 1949, 108 pp.; TOM Reel 259, frames 129–328; FIAT Reel CC–259.

Literature review of the mechanism of the synthesis reaction by way of heterogeneous catalysis, on carbide formation in the treatment of Fe catalysts with CO, and on the thermomagnetic method of studying the carburization of Fe. The composition of Fe catalysts

at various stages of pretreatment and snythesis was determined by chemical and thermomagnetic analysis. The latter method revealed the almost complete transformation of Cu-free Fe catalysts, carburized at 325°, to a ferromagnetic higher Fe carbide (Fe_2C) with a Curie point of 265°. Carburization of Cu-promoted (20% Cu) Fe catalysts at 220°–230° yielded not only the Curie point 265° carbide but also a second ferromagnetic Fe carbide whose Curie point was 380°. Of these 2 carbides, the first is the more thermally stable; it reverts to Fe_3C above 400°, whereas the second carbide is unstable above 300°, being ultimately converted to cementite and free Fe above that temperature. The higher Fe carbides formed during carburization were stable during the synthesis. During carburization at 325° and during subsequent medium-pressure synthesis; the Curie point 265° carbide was virtually the only carbide present. After carbide-oxide equilibrium was established, active catalysts maintained their carbide content unchanged. A decrease in catalytic activity was marked by a drop in the carbide content and by an increase in the O content. Fe catalysts with a high Cu content consisted of approximately equal amounts of Curie point 265° and Curie point 380° carbide during operation at atmospheric pressure. These carbided catalysts gave almost quantitative conversion of the CO in water gas with liquid and solid hydrocarbons as the principal products. When a catalyst thus carbided was operated at medium pressure, the maximum synthesis temperature dropped from 220° to 205° for the same conversion capacity. This increase in activity probably was due to the presence of the Curie point 380° carbide, which characterizes atmospheric pressure synthesis. When the synthesis proceeded at a lower temperature, no formation of free C appeared during carburization and synthesis. At the end of the pretreatment process, carbide formation and conversion capacity had reached their maximum values and no further C appeared. (*See* abs. 2239.)

2684. ———. [Chemical and Magnetochemical Investigations of Iron Catalysts Used in Fischer-Tropsch Snythesis. I.] Brennstoff-Chem., vol. 31, 1950, pp. 1–9; Bureau of Mines Tech. Paper 718, 1949, pp. 16–45; Chem. Abs., vol. 44, 1950, p. 3696.

Composition of Fe catalysts used in medium-pressure syntheses was studied by means of acid decomposition. The activity of the catalysts increased with increasing formation of carbide during carburization. In synthesis, the large amount of carbide present after pretreatment decreased during the 1st days of operation to 0.2–0.4 gm. of carbidic C per 10 gm. Fe in an active catalyst. There was a corresponding increase in the O content to 0.1–0.2 gm. per 10 gm. Fe. The catalysts maintained this carbide-oxide equilibrium for months. Acid decomposition of catalysts whose activity had decreased (contraction less than 40%) showed, at most, 0.1 gm. carbidic C per 10 gm. Fe and a correspondingly high O content. (*See* abs. 2683.)

2685. ———. [Chemical and Magnetochemical Investigation of Iron Catalyst Used in Fischer-Tropsch Synthesis. II. Magnetochemical Investigations.] Brennstoff-Chem., vol. 31, 1950, pp. 33–42; Chem. Abs., vol. 44, 1950, p. 4223.

Two Fe carbides, both having the formula Fe_2C, appear in various stages in the preparation and use of Fe catalysts for hydrocarbon synthesis. The more stable form has a Curie point of 265°; the less stable, 380° (there may even be a 3d form with a Curie point near the latter). Determinations of the C content of such carbides by the acid method give only 50% of the value determined by hydrogenation with H_2. In acid decomposition, ½ of the C is liberated in free form. In normal-pressure synthesis at 220°–230°, the 2 Fe carbides are present in equivalent amounts. In medium pressure syntheses with Cu-free catalysts, formed at temperatures above 250°, the 265° Curie-point carbide appears to predominate. However, if the normal pressure mixture of the 2 carbides is used, the synthesis temperature can be lowered from 220° to 200° for equal throughputs, and this catalyst activity is well maintained. Low temperatures of carbide formation and increased Cu content favor the formation of Fe_2C with the 380° Curie point; with an Fe:Cu ratio of 5:1 and a temperature below 200°, this is the predominant carbide. An amount of Fe_3O_4 corresponding to the specific equilibrium conditions is always found in the catalyst. The carbide Fe_3C has not been found as a primary C reaction product in active catalysts. While formation of the Fe_2C is a necessary condition for an active catalyst, and the activity of the catalyst is parallel to the Fe_2C content, the physical structure of the catalyst also is important. The possible role of intermediate reactions in hydrocarbon synthesis is discussed. (*See* abs. 2683.)

2686. Pichler, H., and Reder, R. [Formation of Methanol in the Partial Oxidation of Methane and Ethylene Under High Pressure.] Angew. Chem., vol. 46, 1933, pp. 161–165; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 318–326; Chem. Abs., vol. 27, 1933, p. 2671.

Yield of MeOH increases with increasing pressure and decreasing O_2 content of the starting products. With a ratio of CH_4 or C_2H_4:O_2 of 10:1, about 7% of the theoretical yield was obtained. If the initial O_2 content is below 1%, the partial combustion forms mainly MeOH. The formation of MeOH was favored by the presence of H_2O vapor and CO_2, but decreased in the presence of metallic catalysts. Optimum temperatures for the start of the reactions were found for CH_4 but not for C_2H_4. Apparatus is described for gas reactions at high pressures (400 atm.). For practical purposes the reaction could be carried out either at very high pressures or by recirculation of the stripped reaction products with low O_2 concentrations, or by a combination of both. 10 literature refs.

2687. Pichler, H., and Walenda, H. [Formation of Iron Carbonyl in the Action of Carbon Monoxide Upon Steel.] Brennstoff-Chem., vol. 21, 1940, pp. 133–141; Chem. Abs., vol. 35, 1941, p. 3207.

Literature is reviewed in work arising from projected use of CO and H_2 with alloy steels at 300° and 1,000 atm. The heat of formation of liquid $Fe(CO)_5$ in the equilibrium $Fe+5\ CO=Fe(CO)_5$ was determined as +53.7 kgcal. per mol. at constant volume. Theoretical and actual temperature-pressure relations were determined by use of filings of 0.15–0.30 mm. low-C steel containing S and P in 48-hr. tests with still and flowing CO, containing 10% N_2, at 100°–250° and 300 atm. starting pressure. Maximum action in the tests occurred at 270 atm. and 200° in 2 days in still gas. Equilibrium concentrations of gaseous $Fe(CO)_5$ decreased sharply from 5% to 0.01% with increasing temperature. Tests with alloy steels at 200° and 300 atm. showed the 14.2 and 24.4 Cr steels to suffer no weight losses, while a 2.8% Si steel and one containing 1.22% Cb lost 2–3%. Similar tests at 450 atm. of Cr 14.2 and Ni 0.72% gave no weight loss, but steel containing Cr, 3.18; Mo, 0.64; W, 0.6; and V, 0.12% lost 5–8%. Large and small steel filings, containing 5.0% Ni, lost 10 and 30%, respectively, the carbonyl analysis showing no preferential Ni. Steel of 2.46% Mn lost over 5%. Steel of 2.3% V or 1.22 Cb lost 5–8% and one of 5.3 Al lost 1–1.5%. In tests of nearly 17 days at 6 l. per hr. with rods 40 x 6 mm. diam. in flowing 100% CO at 1,000 atm. and 200°, low-C steel lost 2% in weight. After heat-treatment its loss was around 7%. Gray cast iron lost around 75%, retaining its dimensions with a reduction in apparent density from 7.1 to 2.0 and increasing in C from 2.9 to 16% instead of the expected 10–11%. Metallographic sections showed residual skeletons of phosphide eutectic and ferrite residue. Two series of tests with rods in 100% CO and CO containing 60% H_2 and 10% N_2 at 1,000 atm. and 200° showed that steel of 3.18% Cr plus small amounts Mo, Si, W, and V lost weight but increased Cr and Si reduced the loss; mixed gas attacked these alloy steels less; steels of 14–28% Cr were unattacked by either gas; steel of Cr 18, Ni 8.9, and Ti 0.53% gained weight; steels of 2.8–4.3% Si were attacked strongly, but 15% Si greatly reduced attack; steels of 5–23% Ni were attacked strongly at the lower Ni; steels of 2.5–13.5% Mn were attacked less at higher Mn; a 0.4–0.6% Mo steel was attacked strongly by mixed gas; low Cr–Mo–V steels were attacked strongly by both gases as were steels of 2.3% V and 1.22–3.5% Cb. 26 refs.

2688. Pichler, H., and Ziesecke, K. H. [High-Pressure Hydrogenation of Carbon Monoxide Preferably to Isoparaffinic Hydrocarbons. (Isosynthesis). I.] Brennstoff-Chem., vol. 30, 1949, pp. 13–22; Fuel Abs., 1949, No. 2,913.

Isosynthesis is defined as the high-pressure hydrogenation of CO at pressures exceeding 30 atm., preferably between 300 and 600 atm., and about 450°. ThO_2 has been found to be the best simple catalyst. ZrO_2, CeO_2, and, to a much less extent, Al_2O_3 are suitable also. Gaseous and liquid hydrocarbons are formed in which, for example, the C_4 hydrocarbons are 80–90% of a branched nature. If the pressure is too high (above 600 atm.) and the temperature too low (below 400°), considerable quantities of compounds containing O_2 (most of all MeOH, isobutanol, and dimethyl ether) are formed. At 600 atm. and 450° with ThO_2 catalyst, a yield of about 154 gm. was obtained, which consisted of 34.5% liquid products, 29.3% iso–C_4, 14.7% C_3 and n–C_4, and 18.2% C_1 and C_2 hydrocarbons beside dimethylether. By working in several stages, the yield at moderate pressures could be considerably increased. In circulation experiments the $CO:H_2$ working ratio could be widely shifted in the direction of H_2 consumption.

2689. ———. [High-Pressure Hydrogenation of Carbon Monoxide, Especially to Isoparaffin Hydrocarbons. (Isosynthesis). II. Tests on Composite Catalysts and the Conversion of Dimethylether.] Brennstoff-Chem., vol. 30, 1949, pp. 60–68, 81–84; TOM Reel 279, item 13, frames 789–931.

In the continual development of isosynthesis catalysts, a number of composite catalysts were subjected to thorough investigation. It was found that by adding ZnO to ThO_2 the yield of liquid hydrocarbons was increased, and by adding Al_2O_3 the isobutane yield was increased. The yield of isobutane was especially high when 3% K_2CO_3 was added to the aluminum precipitate of a ThO_2+20% Al_2O_3 catalyst. At 300 atm. and 450°, the yield was about 85 gm. per N m.^{3} of pure gas, or 51% of the hydrocarbons produced. When an alkali-free (ThO_2+20% Al_2O_3) catalyst was used at 600 atm. and 450°, 130 gm. of liquid hydrocarbons plus gasol per N m.^{3} of CO–H_2 mixture were obtained. The yield consisted of 61 gm. of isobutane and 56 gm. of liquid hydrocarbons. With the correct amount of $ZnO:Al_2O_3$, it was possible to replace some of the ThO_2. However, the space-time yield was not obtained. A 4-month, large-scale laboratory test with (ThO_2+20% Al_2O_3) catalyst demonstrated the long life and the regenerabiilty of the isosynthesis catalyst. Some investigation was made of the occurrence of dimethylether in the isosynthesis reaction, particularly with ThO_2. It was found that considerable amounts of isobutane could be produced.

2690. ———. Isosynthesis. Bureau of Mines Bull. 488, 1950, 39 pp.

This bulletin is a translation and revision of the original German paper describing an investigation of the synthesis of branched-chain hydrocarbons. The paper contains data on the development of the catalyst for the isosynthesis, on the effect of temperature and pressure of operation, and on the composition of the products of the reaction. Experimental evidence and speculations concerning the mechanism of the isosynthesis are discussed. The original paper appears on TOM microfilm reel 279, item 13, frames 789–931. (*See* abs. 2688, 2689.)

2691. ———. Isosynthesis Process. Oil Gas Jour., vol. 49, No. 15, 1950, pp. 92, 95, 107–108.

Summary in English of the paper reported in abs. 2688, abs. 2689, and abs. 2690.

2692. Pichler, H., Ziesecke, K. H., and Titzenthaler, E. [Composition of Hydrocarbons From Isosynthesis.] Brennstoff-Chem., vol. 30, 1949, pp. 333–347; Chem. Abs., vol. 44, 1950, p. 815.

Benzine fraction was found to consist predominantly of branched paraffins and naphthenes. The principal synthesis products boiling up to 100° were methylbutane, 2–methylpentane, 2,3–dimethylbutane, 2,4–dimethylpentane, 2–methylhexane, 3–methylhexane, 2,3–dimethylpentane, methylcyclopentane, dimethylcyclopentane, and methylcyclohexane. Small amounts of unbranched paraffinic and naphthenic hydrocarbons were found as well as examples of the quaternary C-atom, neohexane, and homologous heptanes. The olefin and aromatic contents increased with the boiling point. More olefins were formed at low synthesis temperature, 375°, than at the higher, 425°. The octane number, motor method, of the primary benzine was about 80 and could be increased about 12 units with 0.08% by vol. of $PbEt_4$. By the addition of alkylated isobutane and $PbEt_4$, the octane number could be increased to approximately 100.

2693. Pichler, H., Ziesecke, K. H., and Traeger, B. [Oxygenated Compounds, Particularly Alcohols, From Isosynthesis.] Brennstoff-Chem., vol. 31, 1950, pp. 361–374.

Purpose of this work was to investigate the oxygenated compounds formed on isosynthesis catalysts and to establish how their composition depends upon the various catalyst additions, the synthesis temperature, and the pressure. In preparing the products, the synthesis conditions were, in part, intentionally chosen so that fewer hydrocarbons and more oxygenated compounds would be formed. In order to investigate the synthesis products, which were obtained through distillation, it was necessary to separate the oxygenated compounds from the hydrocarbons. This was first attempted by selective solution, but it did not succeed. It was necessary to convert the alcohols into their boric acid and phthalic acid esters, which were then easily separated from the hydrocarbons. The most suitable way to isolate the alcohols boiling up to 160° from the isosynthesis mixture was to separate the nonalcohols through azeotropic distillation with MeOH. The alcohols isolated in this way were fractionally distilled afterwards and characterized on the basis of their physical properties. Aldehydes and ketones, as well as acids and esters, have been determined by their chemical characteristics. The dehydration necessary for precise characterization of alcohols can be well-accomplished by extractive distillation with carbon tetrachloride. The composition of the isosynthesis products shows, that under the reaction conditions by which oxygenated compounds are formed, the alcohols are of the same type as those formed on oxide catalysts in the synthesis of MeOH and higher alcohols. MeOH and isobutanol were found as the chief components besides small amounts of ethanol and propanol as well as traces of isopropanol and tertiary

butanol. The higher alcohols investigated (up to C_7) showed almost exclusively α–branchings. The carbonyl compounds formed in relatively small amounts consisted especially of isobutyraldehyde. The ester fraction was very small. The acid content made up about half of the ester fraction, and isobutyric acid was the chief acid component. Addition of alkali favored up to a certain extent the formation of higher alcohols. ZnO added to the ThO_2 catalyst increased the higher alcohol content. Addition of Al_2O_3 strongly reduced the formation of alcohols at far lower synthesis temperatures than normal, apparently through dehydration, and ethers, in part, appeared as byproducts. An increase in pressure effected an increase in the amount of alcohols, probably because of the prevention of dehydration. Hereby, somewhat greater amounts of alcohols, usually present only in traces, have been formed. Increase in temperature favored dehydration, in fact, the straight-chain alcohols decreased in amount less than the branched and the primary decreased less than the secondary or even the tertiary alcohols. The amount decreased further with decreasing C number. A flow diagram is presented that explains the formation of the oxygenated compounds in the catalytic hydrogenation of CO. A comparison of the oxygenated compounds and the hydrocarbons from isosynthesis makes it appear that alcohols are the probable primary products from which by dehydration and hydrogenation the corresponding aliphatic hydrocarbons are formed.

2694. Pickles, A. T., and Sucksmith, W. Magnetic Study of the 2-Phase Iron–Nickel Alloys. Proc. Roy. Soc. (London), vol. 175, 1940, A, pp. 331–344; Chem. Abs., vol. 34, 1940, p. 5811.

Measurements of magnetic saturation intensity of annealed Fe–Ni alloys were used to demonstrate the existence of a 2-phase field in the Fe-rich part of the system. The phase boundaries were determined at temperatures above 450°, and the relation of the equilibrium phase diagram to the thermal hysteresis observed under normal rates of temperature change was studied. At temperatures less than 850°, the diffusion processes take place very slowly in the Fe–Ni alloy, nevertheless, at 525°, annealing for even 12 hr. leads to a considerable breakdown of the single-phase alloys.

2695. Hoselitz, K., and Sucksmith, W. Magnetic Study of the 2-Phase Iron–Nickel Alloy. II. Proc. Roy. Soc. (London), vol. 181, 1943, A, pp. 303–313; Chem. Abs., vol. 37, 1943, p. 6232.

Earlier method for using the magnetic saturation intensity of annealed Fe–Ni alloys for the determination of the equilibruim phase boundaries is extended. Lower temperatures are examined. The mechanism and kinetics of phase changes are studied. High magnetic fields are employed (16,000 gauss). Various heat treatments are described, being carried out down to 325°. The phase diagram of the system is accurately determined as 525°–325°. The mechanism of the phase segregation from the single phase α state has been studied. Contrary to the usual case, one of the phases crystallies out in its equilibrium concentration while the residue of the alloy progressively and uniformly approaches equilibrium composition. The rate of attainment of equilibrium was determined. It is considered that the lower practical limit of temperature where the equilibrium diagram can be studied by annealing experiments has been reached.

2696. Pier, M. [Hydrogenation and Synthesis.] Oel u. Kohle, vol. 1, 1933, pp. 47–53; Chem. Zentralb., 1934, I, p. 2524; Chem. Abs., vol. 29, 1935, p. 6727.

Fundamental principles of the MeOH synthesis and the hydrogenation of coal and mineral oils are represented with the aid of diagrams.

2697. ———. [Leuna Gasoline.] Automobiltech. Ztschr., vol. 36, 1933, pp. 159–160; Chem. Abs., vol. 27, 1933, p. 4384.

Short review of the hydrogenation process of the I. G. Farbenindustrie, covering the preparation of NH_3, MeOH, gasoline, etc.

2698. ———. [Synthetic Motor Fuels and Oils.] Oel u. Kohle Erdoel Teer, vol. 13, 1937, pp. 622–624; Brennstoff-Chem., vol. 18, 1937, p. 402; Chem. Abs., vol. 31, 1937, p. 8874.

Review of the Bergius and the Fischer-Tropsch processes.

2699. ———. [Gasoline From Coal, Tar, and Petroleum. Development of the German Fuel Situation.] Oel u. Kohle, vol. 38, 1942, pp. 1445–1448; Chem. Abs., vol. 37, 1943, p. 6842.

Historical discussion.

———. *See* abs. 1494, 1495.

2700. Pierce, C., Wiley, J. W., and Smith, R. N. Capillarity and Surface Area of Charcoal. Jour. Phys. and Colloid Chem., vol. 53, 1949, pp. 669–683.

Evidence in support of the view that adsorption by charcoal is due to capillary condensation chiefly rather than to formation of a surface layer, as in nonporous adsorbents. The forces causing capillary condensation at low pressures are of the same type as those that cause multilayer adsorption on a plane surface, but because of the effects of opposite walls they are stronger at a distance of several molecular diameters from the substrate than is found for a plane surface. If capillary condensation occurs, it is not possible to determine the surface area of a porous solid from an adsorption isotherm, and the commonly accepted values are much too large. In capillaries a few molecular diameters in width, the Kelvin equation is not applicable. Retentivity is greater for slightly activated samples than for more highly activated ones.

2701. Pierre, H. [Spontaneous Adhesion of Nascent Iron.] Compt. rend., vol. 229, 1949, pp. 203–205; Chem. Abs., vol. 43, 1949, p. 8322.

Low-temperature reduction of powdered Fe minerals yields Fe that has a strong tendency to agglomerate, whereas nonferromagnetic metals do not behave this way. The attraction between grains of Fe to give agglomerates is due to a weak external magnetic field possessed by each grain and is enhanced by the breakdown of crystalline structure during the reduction.

2702. Piganiol, M. [Synthesis of Molecules With Lubricant Properties.] Bull. soc. chim., vol. 10, 1943, pp. 301–310; Petrol. Refiner, vol. 24, No. 5, May 1945, pp. 111–116; Chem. Abs., vol. 38, 1944, p. 2481; vol. 39, 1945, p. 2864.

Review of the theories of lubrication and the possible sources of suitable raw materials for the production of lubricating oils. One of the best sources seems to be those heavy fractions (200°–300° C.) of synthetic hydrocarbons from Fischer-Tropsch process designated as Kogasin, which are rich enough in higher olefins to be converted into excellent oils by polymerization.

———. *See* abs. 759.

2703. Pignot, A. [Catalytic Process for Preparation of a Methane-Rich Fuel Gas from Manufactured Gas.] Ind. Petrol., vol. 9, No. 36, 1941, pp. 29–35; Chem. Zentralb., 1943, I, pp. 471–472; Chem. Abs., vol. 38, 1944, p. 3111.

This process is based on the transformation of CO according to the equation $CO+3H_2=CH_4+H_2O$. In this way a fuel gas having a heating value of 6,000–7,000 kcal. per m.^{3} can be prepared from manufactured gas, which is a mixture of coal gas and blue gas from coke. Calculations are presented for a plant capable of handling 200 m.^{3} of manufactured gas per hr.

2703a. Pines, H. Isomerization of Alkanes. Advances in Catalysis, Academic Press, Inc., New York, 1948, vol. I, pp. 201–256.

Isomerization of butanes, pentanes, hexanes, heptanes, and higher alkanes are discussed. 45 refs. are given.

2704. PINGAULT, P. [Formation and Decomposition of Cementite.] Compt. rend., vol. 191, 1930, pp. 1007–1008; Chem. Abs., vol. 25, 1931, p. 1193.

Pure cementite, prepared by the action of NaCN upon Fe filings at 650°, was heated in a vacuum at various temperatures and subjected to the attack of HNO_3 (d., 1.2). After 10 hr. at 1,000° only faint traces of graphite could be found. After 1 hr. at 1.075° the cementite was agglomerated, and distinct traces of graphite were found. After 1 hr. at 1,175° the cementite was transformed partly into metallic globules having the microscopic characteristics of gray-cast Fe and partly into a powder, containing much graphite. Below 1,000°, therefore, the pure cementite may be considered very stable, but, as soon as the melting temperature of cast Fe is approached, the decomposition of the cementite becomes rapid. In forming cementite from pure Fe and NaCN in the absence of air, it was found that the cementation of the Fe was negligible at temperatures of 600°–650° and 850°–900°. The same results were obtained in pure and in commercial NaCN. Different results obtained in the presence of air are believed to be due to the carbonizing action of the decomposition products of the NaCN.

2705. ———. [Equilibrium Between Iron–Iron Carbide–Oxygen.] Compt. rend., vol. 192, 1931, pp. 45–47; Chem. Abs., vol. 25, 1931, p. 1727.

Fe–C–O diagram is completed by determining the curve representing the equilibrium between Fe and Fe_3C in mixtures of CO and CO_2. In the apparatus used the gas was passed continuously through a closed circuit. The 50-cc. samples were analyzed chemically with an accuracy of more than 0.5%. The Fe was used in the form of fine wire, which made it possible with a small weight of material to fill the whole tube and obtained a rather large reaction surface. The experiments were carried out at atmospheric pressure. To insure having no false equilibrium due to passive resistance, Fe was carburized in a mixture rich in CO and decarburized in a mixture rich in CO_2. Analysis showed that the 2 methods gave the same results at the same temperature. When a mixture of Fe and C was kept in a limited quantity of O_2 the results varied with the temperature: Above 740° Fe_3C was formed, and CO_2 in the gaseous phase varied from 0–28%; between 740° and 700°, the proportion of CO_2 was 28–42%, and Fe_3C was oxidized to Fe and CO; below 700° the content of CO_2 became high enough to oxidize Fe. The following calculations were made: Between 700° and 1,000°, $CO_2+Fe_3C \rightleftharpoons 3Fe+2CO-14.5$ cal.; $3Fe+C \rightleftharpoons FeC-27.5$ cal.

2706. ———. [Cementite.] Ann. chim., vol. 20, 1933, pp. 371–438; Chem. Abs., vol. 28, 1934, p. 3040.

Cementite (Fe_3C, 6.65–6.70%) containing 0.05% of free C was prepared by heating Fe with NaCN at 600°–650°; it also may be prepared by electrolysis of fused NaCN with Fe electrodes or by passing coal gas or CH_4 over Fe at 850°–975°. Fe_3C reduced by H_2 has a density at 0° of 7.30, is not attacked by H_2 under atmospheric pressure at 450°, is thermodynamically unstable at ordinary temperatures, and begins to decompose near the melting point of cast Fe. The equilibria in the system $Fe–Fe_3C–O_2$ have been studied at 830°–1,000°.

———. *See* abs. 472.

PINKEL, I. I. *See* abs. 3295.

2706a. PINO, P. [Uses of the Oxo Synthesis as a Laboratory Method for the Synthesis of Certain Aldehydic Compounds.] Gazz. chim. ital., vol. 81, 1951, pp. 625–634; Chem. Abs., vol. 46, 1952, p. 7,079.

Advantages offered by the Oxo synthesis in organic chemistry are shown by the results obtained in the preparation of aldehydes by the reaction of olefins with CO and H_2. The method is relatively rapid and gives better yields than can be obtained by classic organic syntheses.

———. *See* abs. 2393, 2401, 2401a, 2401b.

2706b. PINO, P., AND PALEARI, C. [Synthesis of Anilides From Unsaturated Compounds, Carbon Monoxide, and Aniline.] Gazz. chim. ital., vol. 81, 1951, pp. 646–653; Chem. Abs., vol. 46, 1952, p. 7,063.

Synthesis of anilides is analogous to that of Oxo synthesis. As in Oxo synthesis and syntheses of esters $HCo(CO)_4$ may be the actual catalyst of the reaction of unsaturated compounds, CO, and aniline. For a given temperature and pressure, the rate of absorption of CO in the formation of anilides is intermediate between that for Oxo synthesis and that for the synthesis of esters.

2706c. PINO, P., ERCOLE, R., AND MANTICA, E. [Synthesis of Esters From Olefins, Alcohols, and Carbon Monoxide.] Gazz. chim. ital., vol. 81, 1951, pp. 635–645; Chem. Abs., vol. 46, 1952, p. 7,062.

Reactions between cyclohexene and various primary, secondary, and tertiary alcohols were studied to gain information on the range of applicability of this method of synthesis and to explain its mechanism. The work indicates that the synthesis of esters from olefins, CO and alcohols is a slower reaction than the Oxo synthesis. The mechanism probably involves scission of the addition compound of Co hydrocarbonyl and olefin by the alcohol.

PIONTELLI, R. *See* abs. 2394.

2707. PIRSON, M. [Production of Gasoline From Coal.] Rev. ind. minerale, No. 394, 1937, pp. 249–263; Chem. Abs., vol. 31, 1937, p. 5538.

Development of the process of coal hydrogenation is reviewed. The net cost of motor fuel produced by this process, or by the Fischer-Tropsch process, is estimated as approximately 20 pf. per l. It is claimed that the synthetic motor-fuel industry could not exist without Government subsidies, but development of processes would be important in case of war.

PISARZHEVSKAYA, N. P. *See* abs. 2890.

2708. PITAVAL, R. [Hydrogenation in France.] Echo mines et met., 1938, p. 487; Coal Carbonisation, vol. 5, 1939, p. 49.

Output of the older French plants for the manufacture of synthetic petrol is to be augmented by several new establishments, the annual output of which is apparently to range 30,000–100,000 tons of petrol. Apart from importation of petrol, the importation of crude petroleum for refining and for the hydrogenation of residues will continue to be normal practice, but the synthetic manufacture is to be developed to meet emergencies. The national resources of coal and lignite do not permit such development as in Germany, where the present production of nearly 1,000,000 tons of synthetic petrol per yr. is to be quintupled within the next 3 yr.

PITZER, K. S. *See* abs. 3589.

PIZZO, M. *See* abs. 748.

PLANTS, K. D. *See* abs. 3305a.

PLATE, A. F. *See* abs. 1705, 1706.

2709. PLATONOV, M. S., TOMILOV, V. I., AND TUR, E. V. [Catalytic Properties of Rhenium. VI. The Decomposition of Methanol Over Rhenium.] Jour. Gen. Chem. (U. S. S. R.), vol. 7, 1937, pp. 1803–1804; Chem. Abs., vol. 31, 1937, p. 8341.

When MeOH is passed over ordinary Re catalyst, it is completely decomposed and almost no CH_2O is obtained. If the catalyst is partly poisoned by H_2S or As_2O_3, good yields of CH_2O result.

2710. PLOTNIKOV, V. A., AND IVANOV, K. N. [Decomposition of Methanol in Presence of the Zinc–Chrome Catalyzer.] Jour. Chem. Ind. (U. S. S. R.), vol 6, 1929, pp. 940–943; Chem. Abs., vol. 24, 1930, p. 3984.

In the synthesis of MeOH from water gas, the reaction is reversible, and the most active catalyzers favor MeOH decomposition as well as its synthesis. A study is made of the decomposing action of the catalyzer $ZnO–Cr_2O_3$ at ordinary atmospheric pressure on the MeOH already formed. The molecular proportion of ZnO to Cr_2O_3 was 10:1. The catalyzer was precipitated on Fe-free asbestos to increase its surface. The precipitation should be effected by Na_2CO_3 from the solutions of the nitrates of the metals; when precipitating by NH_3, the catalyzer obtained is considerably less active. After the precipitation, the carbonates are reduced by H_2. Care must be taken to avoid excessive rise of temperature during the preparation of the catalyzer. The proportion of pure catalyzer to asbestos was 1:1, the total weight of both being 9.5 gm. *Apparatus.*—The MeOH from a burette entered a V-shaped glass tube heated in an oil bath to 150° where it evaporated and its vapors passed into a decomposition apparatus where they were first heated, then filtered through the catalyzer. The products obtained were cooled to liquefy and separate the undecomposed MeOH, the volume of which was measured in a burette, and the gases were collected in gasometers filed with acidified H_2O. *Influence of temperature and speed.*—The first bubbles of decomposition gas appear at 240°–250°; with increase in temperature their quantity gradually increases and becomes particularly noticeable at 275°–280°; at 300° the decomposition is already very intensive. It was found most convenient to pursue the investigation at 325°, the speed of passing in MeOH being 0.125 gm. per min. At a greater rate of speed and at a higher temperature, for example, 335°–350°, a change takes place in the character of the decomposition and of the catalyzer itself, the MeOH decomposing 5 times faster than at 320°–325° while noncondensable white gases are emitted; these vapors are products of HCHO polymerization, whereas the condensed product is trioxymethylene; the catalyzer blackens and a gray ring of volatilized Zn is formed, Zn being reduced at about 340°–350°. Under normal conditions of speed and temperature the condensate consists chiefly of MeOH, whereas the gases consist of H_2, CO, and CO_2. *Stability of catalyzer.*—In agreement with the findings of Smith and Hawk (abs. 3210) and contrary to the statements of Taylor and Kistiakovskii (abs. 3336) and of P. V. Zimakov (Jour. Chem. Ind. (Russia), vol. 5, 1928, p. 1072), the CO_2 formed does not act as catalyzer poison, although it is strongly absorbed by the catalyzer. The catalyzer is very stable and after 57 hr. of uninterrupted work shows no sign of fatigue.

2711. ———. [Synthesis of Methanol From Carbon Monoxide and Hydrogen Under Pressure.] Jour. Chem. Ind. (U. S. S. R.), vol. 7, 1930, pp. 1136–1145; Chem. Zentralb., 1931, I, p. 2143; Chem. Abs, vol 25, 1931, p. 4218.

Object of the investigation was the preparation of MeOH from CO and H_2 under high pressure with the use of catalysts. The synthesis was carried out in a circulating system with a pressure decreasing from 170 atm. in an apparatus presenting no novel mechanical features. The activity of Zn–Cr catalyst begins at 315°–320° and attains a practical speed of condensation at 330°. The highest activity was displayed by Zn–Cr in the proportion of 4:1, while any decrease in Cr reduced the efficiency of the catalyst. The results obtained with various thicknesses of the layers of catalyst do not show any regularity, from which is inferred that such changes, besides influencing the speed of condensation, also affect the character of the process. Dilution of the reacting gas mixtures with H_2 reduces the speed of reaction. Increase of temperature accelerates the general course of the process: At 360° CH_4 predominates, while at 400° higher hydrocarbons take its place. The Zn–Cr catalyst becomes readily poisoned. Precipitated on asbestos, it seems to possess a more highly active surface, tending also to an excessive formation of higher hydrocarbons. ZnO is less active than Zn–Cr. Addition of UO_2 to ZnO does not change the activity of the latter. All catalysts containing Zn tend to the formation of gaseous products, such as CH_4 and higher hydrocarbons with separation of H_2O and contamination of the gases with CO_2. Some CO is reduced to C with formation of soot. The liquid condensate consisted of oil and water layers, the former comprising up to 10% of the bulk. The aqueous layer contained up to 12% of MeOH, 15% EtOH, MeCOEt, and iso–BuCHO. With a Cu catalyst obtained by precipitation of $Cu(NO_3)_2$ and reduction to Cu, the activity begins at 280°, drops at higher temperatures, and becomes again stable at 305°–310°. Addition of 5% of Ag increases the activity of Cu, while addition of Zn–Cr increases the activity very highly, the reaction beginning at 240°. Of all the composite catalysts containing 3 elements, $Cu–ZnO–Cr_2O_3$ in the proportion of 91:8:1 proved most active, supporting the reaction with enough speed at 250°. Precipitation of a mixed solution of all 3 salts and subsequent reduction of the hydroxides produces a much more active catalyst than a mixture of separately prepared metals. Increase of temperature speeds up the process, while dilution of the reacting gas with H_2 reduces the speed. The Cu catalyst with decreased temperature tends to increase the formation of liquid products, however, without any oil. The condensate contains 85% MeOH, EtOH, and H_2O, while the gas is mostly CH_4. No formation of free C was observed. At 250°–265°, the process proceeds to complete conversion of CO. In these tests under the condition of falling pressure, the yield based on CO reached up to 70% when the condensate contained about 85% of MeOH.

2712. ———. [Methanol Catalyzers.] Jour. Gen. Chem. (U. S. S. R.), vol. 1, 1931, pp. 826–844; Chem. Zentralb., 1932, II, p. 1393; Chem. Abs., vol. 26, 1932, p. 3774.

Synthesis of MeOH from CO and H_2 was studied at pressures up to 162 atm., with high speed of reaction gases through the apparatus and temperatures up to 320°, in the presence of various catalysts. Cu is a weak catalyst for MeOH; ZnO possesses good activity, but at high speed of gas flow mostly hydrocarbons are formed in its presence; Cr_2O_3 promotes the reaction: $2CO+2H_2=CH_4+CO_2$. The addition of ZnO to Cu produces no appreciable effect, while the addition of Cr_2O_3 to Cu has a decided favorable effect on the catalysis of MeOH. Like ZnO, Cr_2O_3 becomes ineffective at high speed of reacting gases, and instead of MeOH, hydrocarbons are produced. The combination of Cu, ZnO, and Cr_2O_3 forms an active MeOH catalyst.

2713. ———. [Pyrophoric Character of Some Copper Catalysts for Methanol Synthesis.] Jour. Gen. Chem. (U. S. S. R.), vol. 4, 1934, pp. 1003–1005; Mem. Inst. Chem., Ukrain. Acad. Sci., vol. 1, 1934, pp. 127–131; Chem. Abs., vol. 29, 1935, p. 2062.

Admixture of 2% ZnO or Cr_2O_3 increases the stability of the Cu dispersion formed during the process of its reduction from CuO. The ability, on contact with air, to form spontaneously centers of oxidation and the extension of this process is associated with the presence on the surfaces of adsorbed H_2 in the active state. The preparation obtained by reduction with CO is similar to that from H_2. The pyrophoric process converts the Cu principally to Cu_2O.

2714. PLOTNIKOV, V. A., AND KAGANOVA, E. M. [Decomposition of Methanol in Presence of Copper Catalysts.] Jour. Chem. Ind. (U. S. S. R.), vol. 7, 1930, pp. 672–674; Chem. Abs., vol. 26, 1932, p. 81.

Pure Cu as catalyst is very active, but the degree of activity and stability of the catalyst vary with the kind of initial material: a catalyst prepared by reduction of Kahlbaum CuO wire loses its activity when heated 15 min. to 300°, while that obtained from Merck's CuO granules can stand 3 hr. at 350° without injury. 94% molecular CuO+6% molecular V_2O_5 reduced at 200° 3.5 hr. by H_2 gives a highly efficient catalyst, effecting 100% decomposition at 230°–240°, but, besides H_2 and CO, CO_2 and CH_4 are generated; for synthesis this catalyst cannot, therefore, be of use. Activation of catalysts by addition of ZnO and Cr_2O_3 gives the best results with 90% molecular CuO, 8% molecular ZnO, and 2% molecular Cr_2O_2. Increase in Cr_2O_3 effects a decrease in activity; 100% decomposition was obtained at 200°–210° with CO_2 and CH_4 amounting to about 1% each. Addition of Cd to this catalyst lowers its efficiency to a negligible quantity.

2715. Plotnikov, V. A., and Pospekhov, D. A. [Hydrogen Adsorption on Methanol Catalysts.] Mem. Inst. Chem., Ukrain. Acad. Sci., vol. 1, 1934, pp. 153–167 (in German, pp. 169–170); Chem. Abs., vol. 29, 1935, p. 7741.

H_2 adsorption was studied on a Cu–ZnO–Cr_2O_3 catalyst reduced in H_2 at 200°–300° and still containing bound water. In the range 200°–300, a higher temperature of evacuation increases subsequent H_2 adsorption (removal of more adsorbed H_2O). Successive adsorption and desorption lead to a greater mass of adsorbed gas each time. Saturation is reached only above 1 atm. The catalyst evacuated at 300° (anhydrous) shows lower but completely reversible adsorption. Fatigue is held to be due to dehydration. Adsorption is greater in catalysts rich in ZnO–Cr_2O_3; these also show fatigue most rapidly. No direct simple relation exists between the adsorption of H_2 and the activity at a given temperature. The effect of the temperature of evacuation on the H_2 adsorption is very slight for a 91% Cu catalyst, only 10% from 225° to 300°, but very great for catalysts of lower Cu content, 2.5 times from 225° to 290° for a 60% Cu catalyst. Heat of adsorption is about 1,500 cal. per mol. of H_2.

2716. Plotnikov, V. A., Ivanov, K. N., and Pospekhov, D. A. [Complex Catalysts for the Synthesis of Methanol.] Jour. Chem. Ind., (U. S. S. R.), vol. 8, 1931, pp. 472–478; Chem. Abs., vol. 25, 1931, p. 5139.

Study of the catalytic synthesis of MeOH from CO and H_2 was continued. The possibilities of further activation of the complex catalyst Cu–ZnO_2–Cr_2O_3, the catalytic action of the individual components, and their substitution were investigated. The procedure was the same as that in the former experiments; the reaction was carried on again under the conditions of falling pressure, which begins with the inception of the reaction at a certain temperature. Conclusions.—Cu alone is a poor catalyst; Cr_2O_3 alone is more energetic than Cu, effecting the reaction at 265°, the main reaction proceeding thus: $2CO+2H_2=CH_4+CO_2$. Addition of ZnO to Cu somewhat increases the activity and so does the addition of Cr_2O_3, but the temperature of reaction is reduced to 265°–285°, with formation of a considerable amount of MeOH. Addition of both ZnO and Cr_2O_3 doubles the activity and the conversion of CO into MeOH, as compared with Cu containing only either ZnO or Cr_2O_3. The effect of the combination of ZnO and Cr_2O_3 with Cu does not constitute a simple sum of their influences as individual components. The complex catalyst Cu–ZnO–Cr_2O_3 is considered as a system in which the individual influences of the components are merged to create a specific MeOH catalyst. Addition of Na_2CO_3, Ag, and MgO led to impairment of the activity of Cu–ZnO–Cr_2O_3 and the reaction products.

2717. ———. [Synthesis of Methanol in Presence of Copper, Zinc Oxide, and Chromic Oxide Catalysts.] Jour. Chem. Ind. (U. S. S. R.), vol. 8, 1931, pp. 119–126; Chem. Abs., vol. 25, 1931, p. 5661.

Results of experiments show that the optimum proportions of ZnO:Cr_2O_3 with respect to activity are 11:1; to reach the highest activity they have to constitute 30% of the catalyst. Conversion of CO into combustible liquids (mostly MeOH) is highest at ZnO: Cr_2O_3=8:1 and 60–70% Cu$^-$, but the quality of the products is highest at 55% Cu$^-$. The velocity of the reaction increases with excess of H_2; the yield of MeOH and other combustible liquids also is increased, and the % CO_2 is decreased. The best temperature is 265°; above 280° the quality of the products of reaction is lowered considerably; below 250° the velocity is too low. The maximum of CO conversion, that of activity of the catalyst, and that of its stability, do not coincide. The stability is increased by addition of Na_2SiO_3 but the catalytic qualities are lowered.

Podgurski, H. H. *See* abs. 2010.

2717a. Podgurski, H. H., and Emmett, P. H. Adsorption Studies on Iron. Am. Chem. Soc., 121st Meeting abs., March–April, 1952, p. 29–N.

Adsorption characteristics of various Fe catalysts and Fe samples for H_2 and CO have been evaluated from 10^{-2} to 700 mm. Hg pressure between —195° and —200°. No evidence could be found on bulk Fe catalysts for the "solubility" effect noted by Beeck and coworkers for H_2 in thin metal films of Fe and Ni between —195° and 0°. On no surface studied was the activated adsorption of H_2 at —195° sufficient in quantity to cover the free Fe surface with a layer of H atoms; however, for a singly promoted Fe catalyst (2–10% Al_2O_3), the rapid adsorption of H_2 at —195° was equivalent to adsorption as atoms on about ⅔ of the "free Fe surface". Type B activated adsorption of H_2 on promoted Fe catalysts at and >100° is very pressure-sensitive, and at a pressure of 10^{-2} mm. Hg apparently becomes very small relative to Type A adsorption (chemisorbed at —78°). The chemisorption of CO at —195° to —78°, which seems to be satisfactory for measuring the free Fe surface of catalysts and thin evaporated Fe films, covers only about 10% of the surface of very pure Fe wire, Fe powder from the reduction of pure Fe_2O_3, and Fe powder from Fe carbonyl. The ratio of Type B H_2 adsorption to Type A appeared to increase as the ratio of promoter to Fe content was increased in synthetic NH_3 catalysts.

2718. Podgurski, H. H., Kummer, J. T., DeWitt, T. W., and Emmett, P. H. Preparation, Stability, and Adsorptive Properties of the Carbides of Iron. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 5382–5388.

Hägg Fe_2C can be formed by carbiding finely divided Fe catalysts with a hydrocarbon such as propane, butane, or pentane equally as well as carbiding with CO. The carbiding process using a hydrocarbon is not accompanied by a lay-down of free C or by any strong exothermicity. The samples of Fe_2C formed by using butane as a carbiding gas still contain a little residual Fe after the carbiding reaction at 300° apparently comes to an end. Only about 7.5% C seems capable of being incorporated by this procedure in the catalyst employed. It is possible to form hexagonal Fe_2C by carefully carbiding an Fe synthetic NH_3 catalyst at about 215° with CO, even though the catalyst does not contain Cu. CO is still chemisorbed by a partly carbided Fe catalyst at —195°, —78.5°, and —46°, indicating that the carbiding proceeds through the formation of nuclei of carbide rather than by the formation of a smooth layer of carbide over the catalyst surface. The formation of carbide eliminates most of the chemisorption of CO at 100° and 200°. It also eliminates the chemisorption of H_2 in the temperature range —78.5° to 0°. On the other hand, it has little effect on the higher temperature type of H_2 adsorption occurring at and above 100° until the catalyst samples are almost completely converted to Fe_2C. The energy of activation for carbiding Fe with CO to form Fe_2C is about 32.5 kg.-cal. per mol.

Podurovskaya, O. M. *See* abs. 1653.

Poll, A. *See* abs. 642.

Pollchik, M. *See* abs. 2100, 2101, 2103a.

Polley, M. H. *See* abs. 1771.

Polozhintseva, E. *See* abs. 2775.

2719. Pomey, J. [Cementation With Carbon and With Nitrogen.] Rev. Mét., vol. 47, 1950, pp. 637–657, 727–738; Chem. Abs., vol. 45, 1951, p. 1929.

Comprehensive review of the latest knowledge of cementation phenomena, giving a review of theories explaining the equilibrium of γ–iron in mixtures of CO, CO_2, CH_4, H_2 in different concentrations followed by their individual analysis. It is held that H_2 is adsorbed during preheating, becomes dissociated on the surface of γ–iron, and decomposes CO, forming nascent C, which alloys with Fe. Influence of type of C on the carburization phenomena was investigated by placing low-C steel specimens embedded either in graphite or in amorphous C in a furnace filled with a carburizing atmosphere and heating at a carburizing temperature. Specimens placed in amorphous C were properly carburized, and those in graphite did not show any case. Formation of graphite in carburized case should be avoided on this account, and curves are given to show temperature leading to formation of graphite and amorphous C. Sugar and cellulose do not produce any graphite on carburization, but polynuclear aromatic compounds such as naphthalene, anthracene, or picene produce macromols on carbonizing, carrying on their periphery C atoms partly composed of graphite. The mechanism of graphite formation is illustrated. Aliphatic hydrocarbons dissociate on pyrolysis into H_2 and free radicals which can recombine with each other or with H_2, C_2H_4 being the principal radical. A maximum C concentration of 0.85% produced by CH_4 can be increased to 1.15% C by using less stable C_2H_6 or C_2H_4 in concentration under 5% or, preferably, 0.5–3.5% C_3H_8. Diffusion phenomena are extensively investigated mathematically, and an equation is developed.

2720. Pomey, J., Coudray, R., and Goutel, F. [Kinetics of the Decomposition of Austenite of the Alloy Iron–Carbon–Nitrogen.] Compt. rend., vol. 230, 1950, pp. 2298–3000; Chem. Abs., vol. 44, 1950, p. 10641.

Study of the isothermal decomposition in the alloy Fe–C–N obtained by gaseous cementation of Fe wire and homogenization shows that N_2 has a considerable retarding effect both on the rate of germination of α–Fe and on the rate of linear crystallization.

2721. Pomey, J., Goutel, F., Moulin, J., and Coudray, R. [Thermomagnetic Transformation of the Iron–Carbon–Nitrogen Alloys.] Compt. rend., vol. 230, 1950, pp. 2196–2198; Chem. Abs., vol. 44, 1950, p. 10641.

Fe–C–N alloys containing up to 1.5 N_2 and 1.25% C were prepared by cementation of 0.5-mm. wires of mild steel heated to 810° in a mixture of CO_2, H_2, and acetonitrile for N_2 content up to 0.6% and a slight addition of NH_3 for N_2 contents 0.6–1.5%. These alloys showed the reversible thermomagnetic transformations of austenite in cementite Fe_3C and nitride Fe_4N. This eutectoid transformation begins at 595°, as in the Fe–N alloys, but it is completed at a lower temperature than the Fe–N and Fe–C alloys.

Pongracz, A. *See* abs. 3373.

Porai-Koshits, E. A. *See* abs. 3414.

Porter, D. J. *See* abs. 2178.

2722. Porter, H. C. Coal as an Auxiliary Source of Gasoline Supply. Chem. and Eng. News, vol. 22, 1944, p. 904.

In connection with a possible shortage of petroleum and natural gas, the possibility is discussed of obtaining gasoline through the conversion of coal into water gas and thence into gasoline by the Fischer-Tropsch process. An estimation is given of the costs in the coal process, and a comparison is made with the cost of gasoline produced in a refinery.

2723. Pospekhov, D. A. [Properties of Methyl Alcohol Catalyst.] Mem. Inst. Chem., Ukrain. Acad. Sci., vol. 2, 1935, pp. 157–173; Chem. Abs., vol. 30, 1936, p. 5734.

Catalyst (60:35.6:4.4=Cu:ZnO:Cr_2O_3) is highly active for 1:2 CO:H_2 mixtures at 192°–230° per 100 atm. At high rates of flow and at 200°–300° the ZnO undergoes reduction, yielding Cr_2O_3 impregnated with brass; the condensate contains little MeOH, the yields of which rise with diminishing rates of flow. The results suggest that a higher Cu content is indicated, in order to prevent local overheating of the catalyst, with its consequent inactivation.

2724. ———. [Role of Copper in Methyl Alcohol Catalysts.] Mem. Inst. Chem. Ukrain. Acad. Sci., vol. 3, 1936, pp. 533–540; Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 173–176; British Chem. Abs., 1937, B, p. 646; Chem. Abs., vol. 31, 1937, p. 4265.

Cu–ZnO–Cr_2O_3=60:35.6:4.4 gives good yields of MeOH from CO and H_2 at 230°, but is rapidly inactivated. Cu–ZnO–Cr_2O_3=82:16:2 is stable but gives higher alcohols in addition to MeOH. Satisfactory results were obtained with a 1:1 mixture of the 2 catalysts, with an initial contact temperature of 200°.

2725. ———. [Synthesis of Methanol at Low Pressure.] Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 24–28; Mem. Inst. Chem., Ukrain. Acad. Sci., vol. 3, 1936, pp. 403–412, in German pp. 412–413; Chem. Abs., vol. 31, 1937, pp. 2165, 5755.

Catalyst 60 Cu: 35.6 ZnO: 4.4 Cr_2O_3 is very active, but it rapidly loses activity when it works above 200°. If the pressure is 40–30 atm., yields of 0.51–0.63 l. of MeOH per hr. per kg. of catalyst are obtained, and the catalyst retains its activity. At higher pressures, larger yields are obtained but catalytic activity drops. The ratio of CO:H_2 can be varied greatly without effect on the process.

2726. ———. [Copper–Zinc–Chromium Catalysts for Methanol Synthesis.] Mem. Inst. Chem., Ukrain. Acad. Sci., vol. 5, 1938, pp. 507–515; Chem. Abs., vol. 33, 1939, p. 5608.

Review of the literature and patents dealing with Cu–ZnO–Cr_2O_3 catalysts for MeOH synthesis, with 43 refs.

2727. ———. [Mechanism of Catalytic Syntheses From Hydrogen and Carbon Monoxide. (Preliminary Report).] Sbornik Nauch.-Issledovatel. Rabot Kiev. Tekh. Inst. Kozhevenno-Obuvnoi Prom., vol. 3, 1940, pp. 261–267; Khim. Referat. Zhur., vol. 4, No. 5, 1941, p. 12; Chem. Abs., vol. 37, 1943, p. 5569.

It is postulated that the primary process of catalytic transformations of the mixture of CO and H_2 consists of the hydration of CO, and of its condensation with the formation of the lower oxides. The properties of the known oxides of C belonging to several homologous series (cyclic structures also are possible) are given. It is expected that the hydration of these oxides forms compounds with the same C lattice.

2728. ———. [Choice of Catalysts for the Synthesis of Methanol From Carbon Monoxide and Hydrogen.] Jour. Appl. Chem. (U. S. S. R.), vol. 20, 1947, pp. 769–772; Chem. Abs., vol. 42, 1948, p. 5410.

Choice of a catalyst for synthesis under high pressure on the basis of its behavior in the decomposition of MeOH under atmospheric pressure is unjustified.

2729. ———. [Comparative Characteristics of Catalysts Used in Synthesis of Methanol.] Jour. Appl. Chem. (U. S. S. R.), vol. 20, 1947, pp. 1182–1184; Fuel Abs., 1948, abs. 4013.

Results of an experimental evaluation of 16 different catalytic compositions described in the literature for the synthesis of MeOH from CO and H_2 are tabulated. A Cu–Zn–Cr_2O_3 catalyst is preferred.

———. *See* abs. 2715, 2716, 2717.

2730. Pospekhov, D. A., and Shokol, A. A. [Effect of Alkali Upon Copper Catalysts for Methanol.] Mem. Inst. Chem., Ukrain. Acad. Sci., vol. 4, 1937, pp. 205–212, in German, pp. 212–213; Chem. Abs., vol. 32, 1938, p. 3244.

Catalysts 60 Cu:35.6 ZnO:4.4 Cr_2O_3 and 16 ZnO:Cr_2O_3:82 Cu containing 0.1–5 mol. % KOH were used in MeOH synthesis from CO_2 and H_2. The catalysts showed great activity at pressures up to 100 atm. and at an initial temperature of 200°. The product consisted chiefly of MeOH and EtOH (22.3% by weight). By increasing the volume speeds the yield of EtOH is increased and MeOH is decreased. The catalyst 82 Cu:16 ZnO:Cr_2O_3 is more suited for EtOH formation and is more stable.

2731. Postlethwaite, J. P., Bardgett, H., and Bondy, H. F. Inspection of Krupp-Lurgi Plants for the Carbonization of Coal at Low Temperatures. BIOS Final Report 616, 1946, 41 pp.; PB 46,390.

Krupp plants at Wanne Eickel and Velsen are described. The coke from the former plant was used for gas generation in the adjoining Fischer-Tropsch plant. Of the 10 Fischer-Tropsch generators, 2 operated on low-temperature coke and 8 on high-temperature coke. The coke was particularly suitable for the production of water gas as the ratio H_2:CO was 1.4:1, as compared with 1.2:1 in the case of high-temperature coke. The tail gases from the Fischer-Tropsch plant were used to heat the low-temperature retorts. The gasoline obtained by scrubbing the low-temperature gas was mixed with that obtained from the Fischer-Tropsch plant and helped to raise the octane number.

Pouillard, E. *See* abs. 2272.

2732. Pourbaix, M. [Heterogeneous Catalysis of Reactions Between Gases, on Reactions Between Gases and Nongaseous Substances, and on the Poisoning of Catalysts.] Bull. soc. belge ing. ind., 1934, pp. 783–817; Chem. Abs., vol. 29, 1935, p. 402.

With the help of the Nernst approximation formula equilibrium calculations are presented for the reaction of O_2, H_2, N_2, Cl_2, and S_2 with metals to form, respectively, oxides, hydrides, nitrides chlorides, and sulfides; the reactoin of H_2O, CO_2, and SO_3 with metal oxides to form hydrates, carbonates, and sulfates, respectively; and of O_2 with metal sulfides to form sulfates and oxides, respectively. Values for the heats of these various reactions are tabulated for many metals. Similarly, equilibrium calculations are presented for the reduction of metal oxides by H_2, CO, and hydrocarbons; particular attention is paid to the reduction of ZnO. The poisoning of catalysts is considered from the standpoint of the partial pressures or ratios of partial pressures of various reactants necessary to convert the catalyst into some noncatalytic compound.

2733. Powell, A. R. Future Possibilities in Methods of Gas Manufacture. Transcript of Federal Power Commission hearings, June 1946, 46 pp.

A comprehensive review of methods and their economic possibilities. It is concluded that the future raw materials for the manufacture of gas in the northeastern part of the United States will continue to be chiefly bituminous coal and heavy fuel oil. High-temperature carbonization will continue to be carried out predominantly in byproduct coke ovens. This process is characterized by relatively high investment cost per unit of gas made, and by high operating credits from coke, tar, and other products. Costs will be decreased by the development of new byproducts, the upgrading and discovery of new uses for present product, increasing capacity and thermal efficiency of present equipment, and cheaper plant construction. The location of high-temperature carbonization plants near the point of gas consumption is more economical than their placement at the coal mine. Low-temperature carbonization of coal has no future interest largely because of low operating credits and a low yield of gas. The carburetted water-gas process using chiefly coke and heavy fuel oil will remain the major method of manufacturing gas for many years to come. The most important potential improvement is an increase in the thermal efficiency owing to the use of O_2 which can now be produced at a reasonable price. Producer gas, because of its low heating value and despite its high thermal efficiency and low cost of manufacture, has no future. Complete gasification processes as recently developed in Germany (Bubiag-Didier, Pintsch-Hillebrand, Schmalfeldt-Wintershall, Winkler, Lurgi, and Thyssen-Galocsy) are not suitable for use in this country. The most promising principle appears to be the complete gasification of powdered coal suspended in a stream of O_2 and steam (an H. Koppers development). Underground gasification as practiced in Russia has little prospect of success in the United States. The manufacture of oil gas, of liquefied petroleum gases, or re-formed natural gas has only limited possibilities locally.

2734. ———. German Developments in the Production of Synthetic Liquid Fuels. Coal Technol., vol. 1, No. 3, August 1946, 6 pp.; Am. Inst. Min. Eng., Tech. Pub. 2096.

Summary of the more important information obtained by the Combined Intelligence Objectives Subcommittee in its investigation of German synthetic liquid fuels activities. A brief description of each of the 2 general processes for synthetic fuel production—the Bergius and the Fischer-Tropsch—with special mention of the more important new developments. Of the peak production of oil fuel of about 1,200,000 metric tons per month, about 29% was synthetic liquid fuel, and, of the 347,000 tons per month of synthetic fuel, 14% was made by the Fischer synthesis and 86% by hydrogenation of coal and tar. The general impression gained by the Technical Oil Mission was that the engineering design of the plants and the operating techniques were neither economical nor efficient and, by American standards, should have produced a much greater quantity of oil than they did.

2735. ———. Gas Manufacture From Fuels Other Than Coal. Gas World, vol. 127, 1947, pp. 116–121; Gas Times, vol. 52, 1947, pp. 164, 167–168, 233–234, 237, 292–294; Gas, vol. 23, July 1947, pp. 75–76.

Discussion of the oil-gas process, carburetted water gas, liquefied petroleum gas, oil carbonization, cracking of bunker C oil, and the Fischer-Tropsch process, the latter from its possible application to the manufacture of gas in conjunction with the manufacture of synthetic oil and the utilization of off-peak water gas to make synthetic oil. Previous economic calculations are reviewed and conclusions drawn. In view of the economic situation and the fact that much development work remains to be done on the conversion of coal into gasoline and gas, the scheme of making gas in conjunction with manufacture of synthetic gasoline does not appear to be an immediate practical possibility. Also the probabilities of utilizing off-peak water-gas equipment for the production of products other than gas are remote. Furthermore, the capital investment in a Fischer-Tropsch plant is far greater than in the water-gas plant used to make the synthesis gas, so we would have the incongruity of building an expensive plant for part-time operation to keep a less expensive plant in full-time operation.

———. *See* abs. 98, 1329, 1330.

2736. Powell, H. M., and Ewens, R. V. G. Crystal Structure of Iron Enneacarbonyl. Jour. Chem. Soc., vol. 61, 1939, pp. 286–292; Chem. Abs., vol. 33, 1939, p. 3651.

Crystal structure of Fe enneacarbonyl, $Fe_2(CO)_9$, prepared by the method of Dewar and Jones (abs. 700) was derived by a Patterson and Fournier analysis differing from that of Brill (abs. 354) and of Sidgwick and Bailey (abs. 3184). Each Fe atom is linked to 3 terminal carbonyl groups and the 2 Fe atoms are joined by 3$>C{=}O$ bridges. Data are based on single crystal oscillation and zero-layer-line Weissenberg photographs about the *a* and *c* axes of thin, hexagonal, crystal plates. The unit cell contains 2 mol., $a=6.45$, $c=15.98$ Å., density=2.08. The space group is $C\,6_3/m$. The interatomic distances are: Fe–Fe, 2.46, Fe–C (in $C{\equiv}O$), 1.9; Fe–C (in $C{=}O$), is 1.8; $C{\equiv}O$ is 1.15; and $C{=}O$ is 1.3 Å. Angle between (OC)–Fe bond is 94°; between Fe–C bonds, 78°; and between bonds of $>C{=}O$, 87°. The structure simultaneously fixes the molecular formula of the compound as $Fe_2(CO)_9$, as no direct molecular-weight determination is available. Its magnetic properties are discussed.

2737. Power, H. H. Petroleum Substitutes: Past and Present Research, Development, and Economics. Petrol. Eng., vol. 18, No. 5, 1947, pp. 70, 72, 75, 78, 80, 82, 84.

Review of the literature on the production of liquid fuels from the hydrogenation of coal, from coal carbonization, from oil shale, from tar sands, and from the Fischer-Tropsch synthesis, with 25 refs. Special emphasis is placed on the economics of the various processes and the discussion on costs is summarized in the table given below.

Process	Est. reserves in U. S.		Size of plant, bbl. gasoline per day	Total investment, million dollars	Investment cost per bbl. gasoline per day, dollars	Operating costs, including depreciation	
	Bbl. oil, billion	Bbl. gasoline, billion				Per bbl. oil, dollars	Per gal. gasoline, cents
Coal hydrogenation		3,100	1,750	50	28,500		[1] 15.5–22.6.
Coal carbonization		322	1,000	4	4,000	0.94	[2] 10.
Oil shale	100		500–540	5.8–5.9	11,600–16,700	1.75–2.00	9.7–10.7.
Tar sands	[3] 275		3,000	8	2,670	.75	(Compete with gasoline from crude oil.)
Fischer-Tropsch:							
European process using coal		4,000	6,000	45.6	7,600		[1] 19.2.
European process using natural gas		15	6,000	28.5	4,750		[4] 8.8.
Future American process using coal		4,000					[5] 6.0.
Future American process using natural gas		15	6,000	20	3,330		[4] 5.25.

[1] Coal at $2.75 per ton
[2] Coal at $1.55 per ton.
[3] Total in Western Hemisphere.
[4] Natural gas at $0.05 per M cu. ft.
[5] Coal at $2.00 per ton.

Pranschke, A. *See* abs. 2623.

Pratje, W. *See* abs. 3052, 3053.

2738. Pratt, T. W. Aromatic Adsorption Index for the Estimation of Surface Area and Catalytic Activity. Petrol. Processing, vol. 2, 1947, p. 946.

Paper presented at the 27th annual American Petroleum Institute meeting in Chicago. The aromatic adsorption index provides a means for rapidly and simply detecting changes in the catalytic surface available and changes in activity owing to the destruction of catalytic surface either by heat or steam. Detailed procedure for the determination of the aromatic adsorption index, as well as experimental data and correlations concerning the effect of variables upon the value, are given, and the steps to be taken in determining the index are described. Correlations of the aromatic adsorption index with activity for type "A" and other synthetic catalysts show the estimated activity of a given sample can be expected to be within + or −2% (conversion) of the true activity. In most cases correlations for catalysts from the same source used in different units under different conditions will be accurate enough for the estimation of activity.

2739. Prax, Y. Synthetic Methanol. Chem. and Ind., No. 34, Aug. 23, 1947, p. 525.

Since 1945, a pilot plant for the synthesis of MeOH by the Lacotte process has been operating at Decazeville, France, by the Société Aveyronnaise de Methanol. The process uses wood as the raw material, and the gas retort, using steam and O_2 injection and operating at about 500°, yields a gas containing, by vol., 30% CO_2, 21% CO, 42% H_2, 3% CH_4, and 4% N_2. CO_2 is removed by water washing at a pressure of 30 kg. per cm.^{2}, leaving a gas containing 30% CO and 60% H_2 with less than 10% of inert gases. To produce MeOH the gas is passed at a pressure of 650 kg. per cm.^{2} and a rate of 750 m.^{3} per hr. over a catalyst consisting of a mixture of Zn and Cr deposited on active charcoal. The temperature in the catalyst tubes is about 425°.

2740. Prchlík, J., and Otta, K. [Determination of Low Concentrations of Carbon Monoxide in Flue Gases by the Combustion Method.] Paliva a voda, vol. 30, 1950, pp. 218–219; Chem. Abs., vol. 44, 1950, p. 11059.

I_2O_5 method has disadvantages: I_2O_5 is hygroscopic; it is very difficult to determine when I_2O_5 is exhausted; the method consumes considerable time; it is difficult to obtain reliable results when CO is above 0.1%. To obviate the mentioned difficulties, the authors designed gas absorption apparatus using a modified combustion method. The flue gases are measured in a 1,000-ml. gas burette containing saturated Na_2S as confining liquid. The gases enter a scrubber with 30% KOH to remove CO_2 and safety wash bottle with 0.005 *N* $Ba(OH)_2$ and then are led over granular refractory material 3–10 mm. in size in a Mars-tube furnace held at about 900°. The products of combustion, with formed CO_2, are absorbed in a series of 3 washing bottles, each one containing 20 ml. 0.005 *N* $Ba(OH)_2$. After the run, the excess of $Ba(OH)_2$ is titrated back with 0.005 *N* oxalic acid to phenolphthalein (0.2 gm. phenolphthalein in 100 ml. 70% EtOH). Before actual determination, the apparatus is flushed with 300 ml.

CO-free air. During the run the gas is bubbled through the tube furnace at a rate of 1–2 bubbles per sec. Ba $(OH)_2$ is titrated back to the first disappearance of color. The sum of the 3 wash bottle titrations gives the total CO content in flue gases. The mixing of Ba $(OH)_2$ during titration is accomplished with CO-free air. The accuracy is ±0.002%; the range, 0.002–0.5%; and the time required, 2 hr.

2741. Prettre, M. [Methane: Reagent for Hydrocarbon Synthesis.] Conf. réunion soc. belge étude pétrole, dérivés et succédanés, Brussels, 1947, 16 pp.; Rev. inst. franç. pétrole et Ann. combustibles liquides, vol. 2, 1947, pp. 131–140, 195–200; Jour. Inst. Petrol., vol. 33, 1947, p. 308A; Chem. Abs., vol. 42, 1948, p. 6084.

Two aspects of the kinetics of contact catalysis are examined: Adsorption and reactions in the adsorbed phase. By interrupting a normal catalytic reaction, cooling the catalyst zone in the presence of the reactants and transferring the cold catalyst, with exclusion of air, to a special apparatus (not described), it is possible to study the gases given off on desorption as the temperature rises, the most loosely adsorbed products being evolved first. A study of the catalyst in the course of catalytic cracking with hydrogenation showed a high concentration of CH_4, although none of this material was present in the feed and only a small amount in the product. It is, therefore, concluded that the adsorbed phase has a high concentration of CH_3, CH_2, and CH radicals; the isomerization process can thus be considered as being one of methylation. In seeking to find a reaction in which the role of CH_4 could be experimentally demonstrated, thermodynamic considerations pointed to the Fischer-Tropsch synthesis as being one in which this effect ought to be evident at atmospheric pressure. Experimental addition of CH_4 to synthesis gas shows that it participates in the reaction. The use of CH_4 decreases the induction period of the Fischer-Tropsch catalyst (during which large quantities of CH_4 are normally produced); a similar effect is obtained by the dilution of the synthesis gas with an inert material, such as N_2. It is considered that the large initial formation of CH_4 normally observed is due to the heating up of fresh catalyst; if the temperature is kept low, then condensable aliphatic hydrocarbons can be obtained almost immediately.

2742. ———. [Conditions for Utilizing Surface-Area Measurements by Adsorption in the Study of Adsorbents, Catalysts, and Their Constituents.] Jour. chim. phys., vol. 47, 1950, pp. 99–103; Chem. Abs., vol. 44, 1950, p. 7615.

Surface-area measurements by low-temperature gas adsorption are useful in studying adsorbents and catalysts. However, in comparing surface area and catalytic activity, cognizance must be taken of the many variables such as catalyst composition, temperature, time of evacuation, and nature of prior chemical treatment that may cause marked variation in the activity per unit surface area.

———. *See* abs. 779.

2743. Prettre, M., Eichner, C., and Perrin, M. Catalytic Oxidation of Methane to Carbon Monoxide and Hydrogen. Trans. Faraday Soc., vol. 42, 1946, pp. 335–340; Chem. Abs., vol. 41, 1947, p. 2225.

Controlled catalytic oxidation of CH_4 to CO and H_2 usually is represented by the equation: $CH_4+\frac{1}{2}\ O_2=CO+2H_2$. Experiment shows, however, that in practice, at temperatures up to 1,500° K, conversion yields corresponding with the values of the equilibrium constants for the above reaction are never obtained. The oxidation results from an initial reaction of complete combustion of part of the CH_4, $CH_4+2O_2=CO_2+2H_2O$, which consumes all the O_2. The residual CH_4, amounting to approximately ¾ of that originally taken, then reduces the water vapor and CO_2: $CH_4+H_2O=CO+3H_2$ and $CH_4+CO_2=2CO+2H_2$. Since these equilibria do not give good yields in the absence of a large excess of oxidants, except at fairly high temperatures, it is necessary to effect catalysis at above 850°, or even 900°, to obtain a product containing not more than traces of CH_4. (*See* abs. 779.)

2744. ———. [Participation of Methane in Synthesis Reactions and in the Conversion of Aliphatic Hydrocarbons.] Compt. rend., vol. 224, 1947, pp. 278–279; Chem. Abs., vol. 41, 1947, p. 3739.

It is evident from the results of experiments performed with a catalyst of reduced Ni base on kieselguhr under ordinary pressure and at a space velocity of 100 and using various mixtures of CO, H_2, and CH_4, that with all the mixtures analyzing at least 50% of CH_4, this gas is consumed in various amounts, small at 190° but increasing until at 175° nearly 1 vol. of it is consumed for each 2 vol. of CO in spite of an excess of H_2 in the mixture of reagents. The work summed up in this paper demonstrates that in the presence of suitable catalysts, CH_4 participates in the Fischer-synthesis reaction and in the conversion of aliphatic chains.

2745. Preuner, G. [Equilibrium Between Iron, Ferrosoferric Oxide, Hydrogen, and Water Vapor.] Ztschr. physik. Chem., vol. 47, 1904, pp. 385–417; Jour. Chem. Soc., 1904, II, p. 317.

According to the equation $3\ Fe+4\ H_2O \rightleftharpoons Fe_3O_4+4\ H_2$, p_1/p_2, where p_1 is the water vapor pressure after equilibrium has been reached and p_2 the H_2 pressure under the same conditions, should be a constant for a given temperature. This was found to be the case at 3 temperatures, 900°, 1,025° and 1,150°, the mean values of p_1/p_2 being 0.69, 0.78, and 0.86, respectively. In these experiments, p_1 was varied between 8.8 and 49.3 mm. The heat effect of the reaction $3\ Fe+4\ H_2O=Fe_3O_4+4\ H_2$, obtained by inserting the values of the equilibrium constants in van't Hoff's equation, is calculated to be 11,900 cal. at 960°, while calculations from calorimetric data give 42,890 cal. When used in calculating the heat of formation of ferrosoferric oxide, the value 11,900 cal. gives a result much more in harmony with Baur and Glaessner's work than does the value of 42,890 cal.

Pribytkova, N. A. *See* abs. 2916.

2746. Prichard, C. R., and Hinshelwood, C. N. Interaction of Hydrogen and Carbon Dioxide on the Surface of Platinum. Jour. Chem. Soc., vol. 127, 1925, pp. 806–811; Chem. Abs., vol. 19, 1925, p. 3411.

At 1,000°, when the pressure of CO_2 is kept constant, the rate of formation of CO increases almost linearly with the pressure of H_2 at least up to 300 mm. At constant H_2 pressure, the rate of reaction is at first proportional to the pressure of CO_2 and then passes through a maximum when the pressure of CO_2 is approximately double that of H_2. Large pressures of CO_2 have a greater retarding influence on account of its relatively strong adsorption by the catalyst. CO has a slight retarding influence. When the reacting gases are in equimolecular proportions, the pressure of each being 100 mm., the course of the reaction is very nearly unimolecular; but this result is to some extent a coincidence. A simple mechanism, which accounts for most of the observed facts, is that reaction occurs when H_2 and CO_2 become adsorbed adjacent to each other on an active part of the surface. It must be assumed also, that the fraction of the active surface covered by CO_2 increases from 0° to 400 mm., while the adsorption of H_2 at these points left free from CO_2 is never very great so that the zone of reaction is in that portion of the H_2 adsorption isotherm where adsorption is more or less directly proportional to pressure.

2747. Priestley, J. J. Technical and Economic Aspects of Liquid Purification. Gas Jour., vol. 265, 1951, pp. 611–616, 618; Gas World, Coking Sec., vol. 133, April 7, 1951, pp. 6–15.

Further discussion of the Manchester liquid purification process, which depends on the following reactions:

(*a*) (i) $H_2S+(NH_4)_2CO_3=NH_4HCO_3+NH_4HS$
(ii) $H_2S+NH_4HCO_3=NH_4HS+H_2O+CO_2$
(*b*) $3\ NH_4HS+Fe_2O_3=Fe_2S_3+3\ NH_4OH$
(*c*) $2\ Fe_2S_3+2\ O_3=2\ Fe_2O_3+6\ S$

The process is quite similar to the American Ferrox process and the German Gluud process. Some approximate costs of liquid purification to 100 grains per ft.^{3} are given and compared with oxide boxes as follows, respectively:

Gross cost, d. per 1,000 ft.^{3} of gas	0.79	0.92
Net cost, d. per 1,000 ft.^{3} of gas	[1].54	.47
Gross cost, £ per ton of S	12.9	8.1
Net cost, £ per ton of S	[1]8.6	4.2

[1] S credited at £4 5 s. per ton.

2748. Pring, J. N. Direct Union of Carbon and Hydrogen at High Temperatures. Proc. Chem. Soc., vol. 26, 1910, p. 55; Jour. Chem. Soc., vol. 97, 1910, pp. 498–511; Chem. Abs., vol. 4, 1910, p. 2111.

Continuation of previous work by Pring and Hutton (abs. 2752). C and H_2 combine at all temperatures above 1,100°. At 1,200° reaction is very slow without a catalyst and estimation of the exact equilibrium value of CH_4 is uncertain. 0.35% CH_4 was obtained after 22 hr. at 1,200°. At 1,500°, an equilibrium value of 0.17% CH_4 was obtained after 2 hr. When the C contained a surface deposit of Pt, 0.56% CH_4 was obtained at 1,200° and 0.30% at 1,500°. Above 1,550°, the % of CH_4 rises with temperature. C_2H_2 changes quickly into CH_4 and C_2H_4 above 1,500°, and the CH_4 formed is comparatively stable. In the decomposition of C_2H_2 at 1,200°–1,400°, C_2H_4 forms and is found to persist. This appears to preclude the possibility of CH_4 arising secondarily as no traces of C_2H_4 were found. The presence of CO seems to have no effect in the synthesis or decomposition of CH_4 at any temperature employed.

2749. Pring, J. N., and Fairlie, D. M. Methane Equilibrium. Proc. Chem. Soc., vol. 27, 1911, p. 305; Jour. Chem. Soc., vol. 101, 1912, pp. 91–103; Chem. Abs., vol. 6, 1912, p. 953.

Reaction between C and H_2 was investigated at high gaseous pressures in order to find the equilibrium values at high temperatures, and to learn the effects of pressure upon the synthesis $C+2H_2=CH_4$. The high pressure greatly hastens attainment of the equilibrium value, even in the absence of a catalyst; disturbance of the equilibrium due to formation of C_2H_4 was greatly diminished by the rapid cooling caused by the water-cooled steel walls of the reaction vessel. The experiments up to 100 atm. were carried out in a pressure furnace, while for those from 100–200 atm. a new form of furnace of smaller capacity was constructed. With pressures between 30 and 50 atm., equilibrium was reached in about 2 hr. at 1,200°–1,300°, and in 15 min. at 1,400°, either with or without a catalyst. At 200 atm. the reaction was still more rapid. This indicates that finely divided C would at still higher pressures unite with H_2 with extreme rapidity, since the reaction is exothermic, thus the method might be used for preparing CH_4 on a large scale. CH_4 is the only saturated hydrocarbon formed between 1,100° and 2,100° with pressures up to 200 atm. In the experiments between 10 and 200 atm., the values of the ratio of the partial pressures of CH_4 and of H_2 were constant, when the same modificaton of C was used. At 1,200°, 0.24% and at 1,500°, 0.07% of CH_4 is in equilibrium with H_2 and graphite. For amorphous C the corresponding values are 0.36 and 0.21% for the metastable equilibrium. Thus, the change of free energy of the transformation of C into graphite increases rapidly between 1,200° and 1,600°. The mean specific heat of amorphous C thus, is higher than that of graphite between 0° and 1,200°. The values of the equilibrium constants obtained in this work will probably give, by calculation, more accurate values of the relative specific heats of C and graphite and of C, H_2, and CH_4 at these high temperatures than could be obtained by any direct measurements.

2750. ———. Synthesis of Hydrocarbons at High Temperatures. Proc. Chem. Soc., vol. 27, 1911, p. 217; Jour. Chem. Soc., vol. 99, 1911, pp. 1796–1811; Chem. Abs., vol. 6, 1912, p. 629.

When pure C in the form of a rod is electrically heated in an atmosphere of H_2 at 1,200°, CH_4 and C_2H_4 are formed, the rate of formation of C_2H_4 being about 0.01 that of the CH_4. No C_2H_2 could be detected. Measurements made of the rate at which C_2H_2 and C_2H_4 react with H_2 to give CH_4 show that enough time was not allowed in the above experiments for any large interaction of C_2H_4 and C_2H_2 with H_2 to occur, so that the formation of the hydrocarbons must have been direct. At 1,400° and at pressures 10–40 cm. CH_4 and C_2H_2 are obtained, the ratio of their rate of formation being about 10:1. At 1,650° CH_4, C_2H_4, and C_2H_2 are obtained; and, as at higher temperatures, the quantity of C_2H_4 is about twice that of the C_2H_2. Pd in contact with the C assists catalytically the formation of CH_4 to the same degree as Pt, while Si has no appreciable effect. As the presence of a highly charged electric field makes no difference in the rate of formation of CH_4 at 1,200°–1,600°, no complication is produced in the reaction by ionization from heated C. The formation of C_2H_4, which has not before been observed at these temperatures, can be detected at 1,200° and 1,400°; it is comparable with the CH_4 formed.

2751. ———. Synthesis of Hydrocarbons at High Temperatures and High Pressures. 8th Internat. Cong. Appl. Chem., vol. 21, 1912, p. 65; Chem. Abs., vol. 6, 1912, p. 3363.

Apparatus is a modified form of the pressure furnace used previously (abs. 2750). The main reaction studied: $C+2H_2=CH_4$. Below 1,000° C and H_2 at 1 atm. react so slowly, even in the presence of Pt as catalyst, that equilibrium values are not reached within any reasonably time. H_2 was brought into contact with a C rod heated to 1,100°–1,600° by passing an electric current through it. The containing walls of the Ni-steel reaction vessel (750 cc.) were H_2O-cooled. The CH_4, yielded at any given temperature of the C rod, corresponded to the equilibrium value for this temperature since CH_4 does not decompose in the colder regions of the apparatus. Furthermore, the amount of C_2H_4 formed as a by-product at temperature below 1,500° is so slight that the reaction $C_2H_4+2H_2=2CH_4$, which takes place in the cooler parts does not appreciably affect results. C_2H_2 first becomes noticeable (0.001%) at 1,650°. Various grades of C and graphite were tried. The Sodeau apparatus was used in analyzing the products. Amorphous C gave higher % CH_4 than graphite. Upon long heating of the former the values dropped owing to the gradual change into graphite. Partly purified amorphous C heated 3 hr. at 1,275°, H_2 at 100 atm., gave equilibrium values: 21.5% CH_4, 0.25% CO, and 0.002% C_2H_4. Pt-coated amorphous C, preliminarily purified in Cl_2, after 2.5 hr. at 1,100°, 20 atm., gave 6.35% CH_4 and 1.1% CO. Acheson graphite, 1,200°, 2.5 hr., 105 atm., 17.5% CH_4 and no CO. Other graphites, 1.6–4.7% CH_4. At 1,200°–1,300° and at 30–50 atm., equilibrium is reached in about 2 hr.; above 1,400°, in about 15 min. The reaction velocity at 200 atm. exceeds by far that at 1 atm. The results are in agreement with the mass action law. At 1 atm. the equilibrium value of CH_4, in presence of graphite, is 0.24% at 1,200° and 0.07% at 1,500°. With amorphous metastable C the values are 0.36% at 1,200° and 0.18% at 1,500°. At *n* atm., the CH_4 pressure is *n* times that at 1 atm. From the data obtained, the authors calculate approximately the heat of reaction for changing amorphous C into graphite, to be 1,480 cal. at 1,200°; 1,950 at 1,300°; 2,450 at 1,400°; and 3,200 at 1,550°. It follows that the mean specific heat of amorphous C above 1,100° is higher than that of graphite, and the difference increased rapidly with the temperature. No saturated hydrocarbon other than CH_4 was produced in any of the experiments.

2752. Pring, J. N., and Hutton, R. S. Direct Union of Carbon and Hydrogen at High Temperatures. Jour. Chem. Soc., vol. 89, 1906, pp. 1591–1601; Proc. Chem. Soc., vol. 22, 1906, p. 260; Chem. Abs., vol. 1, 1907, pp. 178, 550.

Purest C rods on being heated in H_2 gave about 0.25% CH_4 at 1,200°–1,350°. 0.4% at 1,700°, and about 1% at 2,700°. (*See* Bone and Jerdan, Jour. Chem. Soc., vol. 71, 1897, p. 41; vol. 79, 1901, p. 1042.) Traces of C_2H_2 were formed at 1,700°, measurable quantities at 1,800°, 0.88% at 2,000°, 3.35–4.2% at 2,500°, and 2.75–3.03% at 2,700°.

2753. Pritzer, G. G. Production of Synthetic Lubricating Oil by Condensation and Polymerization. Nat. Petrol. News, vol. 38, 1946, pp. 606, 608, 610, 612; Petrol. Processing, vol. 1, 1946, pp. 58–59, 61–64.

General survey of literature and patents on the production of synthetic lubricants. One of the most highly developed processes is the thermal or catalytic polymerization or condensation of unsaturated olefinic hydrocarbons such as C_2H_4. C_2H_2 is catalytically reduced to C_2H_4 and this is polymerized to lubricating oil. Olefins from the Fischer-Tropsch process are used as raw materials. The silent electric treatment of various hydrocarbons and fatty materials also results in the production of lubricating oil.

2754. Privalov, S. I., Chaukavin, M. K., Zueva, V. P., and Ogarkov, N. P. [Synthesis of Gas Suitable for Cementation Operations.] Vestnik metallopromyshlennesti, vol. 19, No. 1, 1939, pp. 85–91; Chem. Abs., vol. 34, 1940, p. 1286.

Gas suitable for cementation of steel was prepared by synthesizing CH_4 from CO, CO_2, and H_2 in the presence of a catalyst comprising pumice stone impregnated with a solution of $Ni(NO_3)_2$ containing 15% powdered Cr_2O_3 and reduced with H_2 at 350°. The life of the catalyst was indefinite provided the temperature did not exceed 500°–600° and its surface remained clean. The temperature in the retort was maintained at 400°. If the starting gas has 4–5 times as much H_2 as $CO+CO_2$, the resulting gas did not have to be scrubbed of the CO_2.

2754a. Probst, R. E., Meyerson, S., and Seelig, H. S. Adsorption and Reaction of Carbon Monoxide on Promoted-Iron Catalysts. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 2115–2116.

In a study of the adsorption of CO on Fe catalysts, it was found that chemical reactions occur that produce Fe pentacarbonyl and CO_2. The adsorption apparatus was of conventional design and was operated at constant pressure. The Fe catalyst was of the usual type used for the synthesis of hydrocarbons from CO and H_2. It consisted of mill scale in powdered form finer than 100 mesh, promoted with 0.5 wt. % K_2O. After reduction with H_2 at 340° under 250 p. s. i., the catalyst was degassed at 450° until a pressure of 1.5×10^{-6} mm. was obtained. The gas used contained 98.4 vol. % CO, 0.1 CO_2, 0.7 H_2, and 0.8 N_2. Four adsorption isotherms were measured at 0°, 25°, 65°, and 108° at 280 mm. pressure. After 144 hr. analysis was made of the gas in the adsorption cell revealing Fe pentacarbonyl and large amounts of CO_2. The results indicate that, at temperatures as low as 25°, CO will react with reduced Fe to form $Fe(CO)_5$. The CO_2 could have been produced by the Fe–catalyzed conversion of CO to C and CO_2. It is also possible that the CO_2, and presumably Fe carbide, were produced by the decomposition of $Fe(CO)_5$.

2755. Procopiu, S., and Farcas, T. [Ferromagnetic Curie Point of Thin Layers of Electrolytic Nickel.] Compt. rend., vol. 198, 1934, pp. 1983–1985; Chem. Abs., vol 28, 1934, p. 4642.

Curie point of 3 such layers 80–400μ thick averaged 370°, as compared with 355°, the average for 3 layers 4–40μ thick. The difference is attributed to the greater internal pressure of the thinner layers increasing the number of particles surrounding each magnetic atom (abs. 1395, 2779).

Proctor, R. A. *See* abs. **2318.**

Prokhorova, Z. M. *See* abs. **280.**

2756. Proteus. Synthetic Gasoline by the Fischer Process. Gas World, vol. 105, 1936, pp. 362–363.

Review of the principles, products, and economic aspects of the Fischer process.

Pruett, H. T. *See* abs. **649.**

Prziza, O. *See* abs. **1012.**

2757. Pshenitsyn, N. N., Sidorov, N. V., and Sternina, D. G. [Ultrasonic Treatment of the Catalyst for Ammonia Synthesis.] Jour. Appl. Chem. (U. S. S. R.), vol. 13, 1940, pp. 76–78 (in German, p. 78); Chem. Abs., vol. 34, 1940, p. 8189.

Treatment of the $Fe_3O_4+3\%\ Al_2O_3+1.5\%\ K_2O$ catalyst with a sound of frequency 555 kilohertz did not increase its activity in NH_3 synthesis under a pressure of 300 atm. Describes apparatus used for the treatment.

Puff, H. *See* abs. **1648a.**

2758. Pursglove, J. Will Coal Help to Meet the Future Ueeds for Gaseous and Liquid Fuels? Petrol. Refiner, vol. 26, No. 11, 1947, pp. 198, 200, 202; Min. Cong. Jour., vol. 34, 1948, pp. 22–24.

Paper presented to the American Gas Association Meeting in Cleveland at a general discussion of the synthesis of oil from coal by the modified Fischer-Tropsch process about to be practiced at the plant of the Pittsburgh Consolidated Coal Co.

2758a. ———. Economic Coal Conversion, Is It Possible? Ohio State Univ., Eng. Expt. News, vol. 23, Oct. 1951, pp. 7, 8, 37–40.

Paper was given at the Second Annual Ohio Mineral Ind. Conf., Oct. 5, 1951. Bergius and Fischer-Tropsch processes are discussed. They are considered to be uneconomic under present United States conditions. The Pittsburgh Consolidated Coal Co., has developed a process by which partial conversion of coal will yield a char residue suitable for boiler fuel and 30–40 gal. of liquid fuel and 1,000 cu. ft. of high-B. t. u. gas per ton. Plant cost will be 10% that of a hydrogenation plant and 15% of a Fischer-Tropsch plant. Chemicals and ash-free C will be produced in the hydrogenation plant rather than gasoline or gas.

2759. Putnam, G. L., and Kobe, K. A. Hydrocarbons From Carbides. Chem. Rev., vol. 20, 1937, pp. 131–143; Chem. Abs., vol. 31, 1937, p. 3867.

Review, with 78 refs., deals with the classification of the carbides and with their preparation and reactions.

Puzitskii, K. V. *See* abs. **792, 799, 800, 801, 802a, 802c.**

2760. Pyhala, E. [Franz Fischer Method for Synthetic Gasoline Manufacture in Germany.] Teknillinen Aikakauslehti, vol. 25, 1935, pp. 396–397; Chem. Abs., vol. 30, 1936, p. 1203.

Methods have been developed for removing the S from water gas, and catalysts that give yields up to 70% of the theoretical have been discovered. Estimates show that a factory with a yearly capacity of 25,000 tons could work economically, two-thirds of its output being gasoline and the rest byproducts.

Pyrcioch, E. J. *See* abs. **3573a.**

Pyzhev, V. *See* abs. **3368.**

Q

Quiggle, D. *See* abs. **1098, 1104.**

2761. Quill, L. L. Chemistry and Metallurgy of Miscellaneous Materials. Thermodynamics. McGraw-Hill Book Co., New York, N. Y., 1950, 329 pp.; Chem. Abs., vol. 44, 1950, p. 5694.

Quinke, F. *See* abs. **2306.**

2762. Quirk, R. N. Combined Intelligence Objective Subcommittee Investigation of Ruhr Synthetic Oil Plants. Preliminary Progress Report. TIIC Rept. 17, 1945, 9 pp. PB 17; Nat. Petrol. News, vol. 37, No. 45, 1945, pp. R 861–864.

Brief description of the conditions and work at several plants interested in synthetic oils, etc. Brief summary of the technical work carried on, such as preparation and purification of synthesis gas; catalyst ovens; catalysts; method of operation of the process; the Oxo process for treating C_{11}–C_{17} olefins to produce aldehydes; coal hydrogenation; the Pott-Broche process and the use of pitch; vapor-phase hydrogenation; the D. H. D. process for dehydrogenating naphthenes; use of propane and butane; carbonization and gasification; Lurgi pressure gasification process; Krupp-Lurgi low-temperature carbonization process; brown-coal low-temperature carbonization by the so-called "Spülgas" process; coke ovens; hard-coal tar and brown-coal tar.

R

2763. Racine, J. [Study of the Reducing Properties of Methane.] Compt. rend., vol. 220, 1945, pp. 823–825; Chem. Abs., vol. 40, 1946, p. 3672.

Reduction of some metallic oxides by CH_4 was studied at temperatures up to 1,100°. The following were reduced: CuO, ZnO, CdO, HgO, PbO_2, Cr_2O_3, MoO_3, NiO, WO_3. The following were not reduced: MgO, CaO, Al_2O_3. MnO is converted to a carbide at 800°. C_2H_2 appears at 825°. Fe_2O_3 is reduced to an unidentified oxide at 400°, and to Fe at 800°; a carbide is formed at 1,050°. C_2H_2 is formed at 800°; C is deposited at 1,000°. Co_2O_3 is reduced to CoO at 450°, and to Co at 800°; a carbide is formed at 1,000°.

2763a. Radančević, M. [Synthesis-Gas Production by Partial Oxidation of Methane.] Nafta (Yugoslavia), vol. 3. No. 12, 1952, pp. 5–11; Fuel Abs., vol. 12, No. 2, 1952, abs. 1485; Chem. Abs., vol. 46, 1952, p. 11,636.

Experiments on synthesis-gas production by partial oxidation of CH_4 over catalysts containing various amounts of Ni on SiO_2 gel are described. Catalysts were prepared by impregnating SiO_2 gel of 2-mm. size with $Ni(NO_3)_2 \cdot 6\ H_2O$ solutions, drying several hours, calcining 1 hr. at 500° in an air stream, and reducing in pure H_2 30 min. at 500°. Catalytic conversions have been carried out in an electric-tube reactor containing 25.4–29.4 cc. catalyst. The optimum conditions for the reaction were: Inlet gas rate, 1.12 liter per min., O_2: CH_4 mol. ratio 0.6 and a temperature of 850°. The optimum amount of Ni on the carrier was 3.2%, a further increase of Ni on the carrier giving no better yields of synthesis gas. Equilibrium conditions from available thermal data have been calculated and presented.

2764. Rademacher, H. [Wintershall-Schmalfeldt Process for Gasifying Crude Brown Coal.] Feuerungstech., vol. 28, 1940, pp. 85–86; Chem. Abs., vol. 35, 1941, p. 6091.

Wintershall-Schmalfeldt process, based on the use of friable raw brown coal, gasifies the small fuel in a circulating stream of synthesis gas charged with the vapor produced by the drying. The combination of synthesis-gas manufacture with drying in suspension, without intermediate separation of dust, is one characteristic feature. Another is heating of the circulating gas stream by regenerators, which are themselves heated by the combustion air being preheated to a high temperature, 1,300° C. This is necessary to cover the heat requirements of the water-gas reaction and to maintain temperatures high enough for gasification, making possible high outputs and the production of gas low in CH_4. An illustration shows the general arrangement of the plant.

2765. Raikes, H. R. Liquid Fuel From Coal. South African Ind. Chem., vol. 3, 1949, pp. 82–89; British Abs., 1949, B, I, p. 852.

Reviews proposed production of liquid fuel from coal deposits at Vredefort, Orange Free State, by a modified Fischer-Tropsch process. The water requirements of the plant, estimated at 7 x 10^6 gas. per day, are high in relation to the local supply. The location of other liquid-fuel plants in catchment areas with a rainfall higher than that of Vaal Basin, is discussed with reference to the water supply and the amount and quality of the coal reserves.

Raineau, A. *See* abs. **110, 111, 112.**

2766. Ralph, H. D. Importance of Domestic Industry Stressed in O'Mahoney Report. Oil Gas Jour., vol. 45, No. 40, 1947, pp. 38–39.

According to the final report of the Senate Petroleum Resources Committee, the first principle of American petroleum policy should be to sustain our domestic supply of petroleum and to maintain the American system of competitive free enterprise at home and abroad. The Nation faces 2 alternatives: (1) To await with hope the discovery of enough petroleum within our boundaries to satisfy our future military requirements, and meanwhile to depend upon foreign oil and trust that war will not cut off our imports; or (2) to take steps to guarantee an adequate domestic supply by promoting the search for new deposits of petroleum within the United States itself and the continental shelf and to continue the present program looking to the manufacture of synthetic liquid fuels to supplement our domestic crude supply. Government facilities can be utilized to promote research in the manufacture of snythetic liquid fuels, but without permitting Government competition with private industry. The committee recommends "bold steps" in the direction of synthetic production as being the answer to national defense and to fears that we are running out of oil, and points out that natural gas, shale, coal, and lignite are available in huge quantities and can be liquefied at costs not too far above that of refining crude petroleum.

2767. Rammler, E. [Semicoke for Gasification.] Gas- u. Wasserfach, vol. 80, 1937, pp. 683–691; British Chem. Abs. 1937, B, p. 1153.

Reviews properties of semicokes from coal and brown coal, and gives the results of gasification trials. Good yields of producer gas of net calorific value 1,300–1,400 kcal./$m.^3$ were obtained, the brown coal product being rather more reactive than coke from coal. Brown coal semicoke also can be used via water gas as a source of H_2 for hydrogenation purposes or of Fischer-Tropsch synthesis gas.

2768. ———. [Utilization of Low-Temperature Coke From Brown Coal and Bituminous Coal.] Gas- u. Wasserfach, vol. 18, 1942, pp. 437–444; British Chem. Abs., 1943, B. I, p. 270; Chem. Abs., vol. 37, 1943, p. 5848.

Application to synthesis gas production is foreshadowed.

Rampton, H. C. *See* abs. 1505.

2769. Randall, M., and Gerard, F. W. Synthesis of Methane From Carbon Dioxide and Hydrogen. Ind. Eng. Chem., vol. 20, 1928, pp. 1335–1340; Chem. Abs., vol. 23, 1929, p. 814.

Equilibrium for the reaction $CO_2+4H_2\rightleftharpoons CH_4+2H_2O$ was determined by the dynamic method at atmospheric pressure and at temperatures 322°–392.5°. The catalysts used were supported Ni catalysts, both unpromoted and promoted by ceria. Space velocities 6–12 were used. Equilibrium was approached from both sides. In studying the forward reaction, ratios of $H_2:CO_2$ of 4 and 2.3 were used. The free-energy equation that fits the data for this reaction is $\Delta F^\circ = -35{,}093+12.38\ T\ln T-0.00415T^2-0.000000025T^3-39.91T$. This equation gives $\Delta H^\circ_{298.1}+ -38{,}401$ cal. and $\Delta F^\circ_{298.1}= -26{,}339$ cal. An observed deposition of C during some of the experiments is accounted for by assuming reaction is thermodynamically possible under experimental conditions prevailing.

2770. Randall, M., and Mohammad, A. Synthesis and Free Energy of Methane. Ind. Eng. Chem., vol. 21, 1929, pp. 1048–1052; Chem. Abs., vol. 24, 1930, p. 333.

Equilibrium in the formation of CH_4 from graphite and H_2 and in the reverse reaction was determined at high temperatures, 1,024°–1,237°. The catalyst was reduced Ni with ceria as a promoter. The free energy and heat of reaction of CH_4 calculated from the experiments agree with the values found from the indirect measurements of Randall and Gerard (abs. 2769). $\Delta F^\circ_{298.1}= -11.573$ cal. and $\Delta H^\circ_{298.1}= -16{,}963$ cal. $\Delta F^\circ= -14{,}343+11.1\ T\ln T\ -0.0081T^2+0.0000006T^3 -51.591T$. Compares and discusses results of other workers at different temperatures.

2771. Randall, M., and Shiffler, W. H. Deposition of Carbon in the Reaction Between Carbon Dioxide and Hydrogen. Ind. Eng. Chem., vol. 21, 1929, p. 941; Chem. Abs., vol. 24, 1930, p. 333.

New equation: $CO_2(g)+2H_2O(g)=C(\text{graphitic})+2H_2O$ is offered as a possible explanation for the results presented by Randall and Gerard (abs. 2769) although the mechanism of the reaction may involve a series of reactions.

Rao, B. C. S. *See* abs. 256a.

2771a. Rapoport, I. B. [Synthetic Motor Fuel From Carbon Monoxide and Water.] Paliva, vol. 31, 1951, pp. 328–337; Chem. Abs., vol. 46, 1952, p. 11,632.

Review of synthesis of motor fuel from CO and H_2O, including reaction temperatures, pressures, and catalysts, as well as physical properties and analysis of products formed.

2772. Rapoport, I. B., and Blyudov, A. P. [Methane Synthesis.] Khim. Tverdogo Topliva, vol. 5, 1934, pp. 625–632; Chem. Abs., vol. 29, 1935, p. 2905.

CH_4 synthesis is effective, using CO and H_2 over a Ni catalyst at 250° at 270° the conversion of CO is 99%. A Ni-Mn catalyst permits of carrying out the reaction at 200°–204°. A considerable amount of CO_2 is formed when the temperature is raised to 250°–280°. A Ni-Mn–Al catalyst at the above temperature promotes the simultaneous formation of CO_2 and CH_4. Mo catalyst promotes CH_4 formation at 350°–400°; this reaction slows down and a considerable amount of CO_2 is produced when the above temperature is exceeded. Addition of Al_2O_3 has almost no effect on the yield of various products. The operations are described in detail, and analytical data are tabulated.

2773. Rapoport, I. B., and Lang, A. [Genesis of Catalyst Skeletons.] Jour. Appl. Chem. (U. S. S. R.), vol. 11, 1938, pp. 1056–1062 (in French, p. 1063); Foreign Petrol. Technol., vol. 7, 1939, pp. 13–26; Chem. Abs., vol. 33, 1939, p. 4115.

Properties of catalyst skeletons, which were obtained by the treatment of alloy (Ni–Co–Al or Ni–Al) with an alkali to remove most of Al, were investigated. The catalyst skeletons are more stable against poisoning with S-containing organic compounds than the precipitated catalysts (oxides). The hydrogenation of caprylene, octyl alcohol, cyclopentanone and 1, 3, 4-xylenol in a current of H_2 at 190°–195° disclosed that the Ni–Co–Al catalyst skeleton is a very active hydrogenation catalyst. The dehydrogenation of cyclohexane and methylcyclohexane over the above catalyst proceeded very effectively at 180°–200°, with pressure or without it. The best products were obtained at 240°–260° but the reaction, in this case, was accompanied by a decomposition reaction. At temperature above 260° (280°–320°), the surface of the catalyst was gradually covered with a C film and the catalyst completely lost its activity. The catalyst cannot be reactivated in the usual manner. The loss of activity is explained by the recrystallation of the crystal lattice of the catalyst skeleton at high temperature. Therefore, the isomerization reaction in the presence of the catalyst skeleton would not proceed to a great extent because: (1) The catalyst rapidly loses its activity at 270°–280° and (2) at this temperature the main reaction is the decomposition reaction. Thus, the catalyst skeletons prepared from Ni–Co–Al and Ni–Al alloys are similar to the precipitated catalysts (oxides) in respect to hydrogenation, dehydrogenation, and isomerization reactions, but the first catalysts are less affected by S-containing organic compounds.

Rapoport, I. B., and Polozhintseva, E. Synthesis of Hydrocarbons From Carbon Oxide and Hydrogen Over Alloyed Catalysts. II. *See* abs. 2775.

2774. Rapoport, I. B., Blyudov, A. P., Shevyakova, L., and Frantzuz, E. [Gasoline Synthesis From Carbon Monoxide and Hydrogen at Atmospheric Pressure. I.] Khim. Tverdogo Topliva, vol. 6, 1935, pp. 221–235; Chem. Zentralb., 1936, II, p. 3967; Chem. Abs., vol. 29, 1935, p. 7617.

Of the catalysts Ni–Mn, Ni–Mn–Al, Ni–Mn–Cu, Ni–Mn–Cr., Ni–Th–Hg, Co–Th, and Co–Mn, the most active were Co–Th, Co–Mn, Ni–Mn–Cr, and Ni–Mn–Al. The method of preparation of the catalyst greatly affects its activity. The reaction temperature is very important to the life of the catalyst. A high temperature yields less solid hydrocarbons, which are deposited on the catalyst. The best temperature is that at which 7–10% CH_4 is formed. The presence of small amounts of NH_3 in the reaction gas increases the yield of gasoline, particularly with catalysts precipitated on fuller's earth. Asbestos carrier yields the best catalysts. 12 refs.

2775. Rapoport, I. B., and Polozhintseva, E. [Synthesis of Hydrocarbons From Carbon Oxide and Hydrogen Over Alloyed Catalysts. II.] Khim. Tverdogo Topliva, vol. 9, 1938, pp. 64–70; Foreign Petrol. Technol., vol. 6, 1938, pp. 215–246, 293–304; Oil Gas Jour., vol. 38, No. 20, 1939, pp. 52–54; Chem. Abs., vol. 32, 1938, p. 9446.

Gas mixture, an average composition CO, 31.7; H_2, 63.08; CO_2, 0.05; O_2, 0.2; and N_2, 4.97%, after purification and drying was passed into a quartz tube filled with a catalyst, then into a graduated receiver cooled with ice, on to a charcoal scrubber, and then into a gasometer. A portion of the gas was withdrawn for the analysis. The quartz tube was kept at 165°–220°. Ni–Al, Co–Al, and Co–Si catalysts were used in the powdered and granular forms. The Ni–Al catalyst reduced in the H_2 atmosphere at 350° yielded 140 cc. per $m.^3$ (of gas) of hydrocarbon under the optimal conditions: vol. velocity 166 at 170°. The Co–Al catalyst, reduced with H_2 in the NH_3 atm. at 220°, yielded 175 cc. per $m.^3$ (of gas) hydrocarbon at 200° and vol. velocity of 83. The Co–Si catalyst, reduced as the Co–Al catalyst, yielded 109.6 cc. per $m.^3$ (of gas) hydrocarbon at 220° and vol. velocity of 59. All the above data are given for the catalysts in the granular form; the yield of hydrocarbon using powdered catalysts was somewhat lower.

2776. Rasmuson, A. [Production of High-Purity Oxygen and Its Uses in Chemical Industry.] Tek. Tid., vol. 78, 1948, pp. 155–159; British Abs., 1948, B, I, p. 390.

Modern German and American processes for the manufacture of O_2 by fractionation of liquid air are described. The Linde-Fränkl plant, using a Fränkl corrugated Al heat exchanger, provides O_2 of 98% purity at a cost of 0.64 kw.-hr. per $m.^3$; the American plant using a Collins tubular heat exchanger, provides O_2 of 99.5% purity at a cost of 0.5 kw.-hr. per $m.^3$ The main outlet for this cheap O_2 is in the manufacture of synthetic fuel gases. Water gas is made from lignite, steam, and O_2 in a Winkler generator or from coke breeze in a Thyssen-Galocsy generator. The American Hydrocol process utilizes O_2 for the partial combustion of natural gas to yield liquid petroleum fuels. The use of O_2 also is being considered for the underground gasification of coal.

2777. Ratcliff, J. D. All the Gas We Need. Collier's, Nov. 24, 1945, p. 16.

Pilot plant, built by Hydrocarbon Research, Inc., for the production of gasoline from natural gas by the Fischer-Tropsch process, has operated so successfully that a $15,000,000 commercial plant is to be constructed this year at Carthage, East Texas. This plant when completed will produce 5,000 bbl. of 80-octane gasoline, 1,000 bbl. of Diesel oil, and 200,000 lb. of crude alcohols per day. The plant will consume 65,000,000 $ft.^3$ of gas and 40,000,000 cu. ft. of O_2 per day. The process as developed obtains the necessary synthesis gas in the right proportions of $CO:2H_2$ by burning CH_4, natural gas, with O_2. The O_2 for the process is produced, it is said, for $0.05 per 1,000 cu. ft., this low cost being made possible by utilizing the exothermic heat from the Fischer converter in heat exchange relation to produce the power for operating the compressors and other equipment in the O_2 plant. It is expected that the cost of the gasoline will compete with that produced from petroleum.

2778. Ravizza, G. [Refinery Gas as a Source of Methane.] Atti III° convegno naz. metano, vol. 2, 1941, pp. 301–305; Chem. Zentralb., 1942, II, p. 1988; Chem. Abs., vol. 38, 1944, p. 3460.

Dependent upon raw material used and the methods of refining, refinery gases have a variable composition but consist predominantly of CH_4 and contain no hydrocarbons with more than 6 C atoms. Cracked gases contain, relatively, many unsaturated hydrocarbons, and hydrogenated gases virtually none. Modern processes for treating refinery gases are discussed. Gas with S removed, freed from gasoline, butane, and propane, consists essentially of CH_4 and can either be compressed and used as fuel gas or used for the preparation of H_2. The economic fundamentals of getting CH_4 from refinery gas are discussed.

2778a. Ray, J. N. Possible Synthetic Petrol Industry in India. Jour. Indian Chem. Soc., vol. 28, 1951, pp. 53–58; British Abs., 1951, B. I, p. 1052.

It is concluded from a survey of the suitability of the coal resources of India that the production of synthetic fuels from coal would not be an entirely uneconomical process.

2779. Ray-Chaudhuri, D. P. [Displacement of the Curie Point for Nickel by Pressure.] Ztschr. Physik, vol. 71, 1931, pp. 473–477; Chem. Abs., vol. 26, 1932, p. 3154.

In the Curie point of a Ni wire under tension agreement with the Heisenberg theory of ferromagnetism is found. There is agreement between the curves of temperature against temperature coefficient of resistance and against extension, and there also is similarity with the curve obtained between temperature and specific heat for a ferromagnetic substance.

Rayet, R. *See* abs. 1647.

Raynor, G. V. *See* abs. 1517.

Read, A. A. *See* abs. 88, 89.

Réant, R. *See* abs. 62.

Reder, R. *See* abs. 1038, 1039, 2686.

2780. Reed, F. H. Chemical Aspects of Coal Utilization. Univ. Illinois Eng. Exp. Sta., Short Course in Coal Utilization, Circ. 31, 1937, pp. 159–175; Coal-Heat, vol. 32, No. 3, 1937, pp. 56–60; Chem. Abs., vol. 32, 1938, p. 6027.

Review dealing mainly with coal as a chemical raw material and as a source for liquid fuels. Discusses 3 general methods for producing liquid fuels from coal: (1) Carbonization or destructive distillation, (2) direct liquefaction through destructive hydrogenation (Bergius process), (3) synthesis from the products of coal and coke gasification (Fischer process). Hydrogenation of coal seems to be preferred at present over the Fischer synthesis from CO and H_2. It is not probable that commercial production will be undertaken in the United States until the cost of motor fuels from petroleum approaches the cost of making these fuels by synthetic means.

2781. ———. Synthetic Liquid Fuels. Opinion and Comment, University of Illinois Bureau of Economic and Business Research, May 1948; Mines Mag., Colorado, vol. 38, September 1948, pp. 23–25, 34, 36; October 1948, pp. 23, 24.

Review covering developments in the United States with some consideration of the plant requirements in establishing a synthetic fuels industry. Also presents cost estimates.

2782. Reed, R. M., and Eriksen, A. Hydrogen and Synthesis-Gas Production. Petrol. Processing, vol. 3, No. 10, 1948, pp. 1011–1016; Petrol. Eng., vol. 20, No. 1, October 1948, pp. 278, 280, 282, 284, 290; Gas, vol. 24, No. 10, 1948, pp. 53–56; California Oil World, vol. 41, No. 16, 1948, pp. 3, 5, 7, 9, 11; Chem. Abs., vol. 42, 1948, p. 9097.

Paper presented before the California Natural Gasoline Association, August 5, 1948. Reviews status of the hydrocarbon-steam process for manufacturing H_2 and mixtures of H_2 and other gases for various purposes, from natural gas, light hydrocarbons, and steam. Gives an account of the application of the process to the hydrogenation of various petroleum materials, the synthesis of NH_3, the production of high-purity H_2 and $CO–H_2$ mixtures by the Girbotol methods for use in fuel synthesis processes, and for producing gas mixtures suitable for supplementing manufactured gas.

Reed, W. A. *See* abs. 2110.

2783. Refiner. Synthetic Lubricating Oils by Transformation of Chlorinated Hydrocarbons. Vol. 16, 1937, pp. 92–93.

Suitable paraffin wax is obtained from petroleum from low temperature carbonization of coal tar, lignite tars, or directly from waxy products of the Fischer-Tropsch synthesis. Chlorination is carried out by passing Cl gas at maximum temperature through melted wax with I as catalyst.

2784. Regner, A. Magnetometric Determination of the Curie Points. Jour. Iron Steel Inst. (London), Advance Copy, No. 6, 1930, 22 pp.; Chem. Abs., vol. 24, 1930, p. 5695.

A low-frequency magnetometer and 2 high-frequency magnetometers suitable for detecting transformation points in steel are fully described. These instruments gave clear indications of the A_2 point and cementite changes both at 60° and 210°. Irregularities were observed at the temperature of the pearlitic change.

2785. Reich, S., and Serpek, H. O. [Some Reactions of Calcium Hydride.] Helv. chim. acta, vol. 3, 1920, pp. 138–144; Chem. Abs., vol. 14, 1920, p. 1302.

Pure dry CO is passed over Ca hydride heated to a dark-red heat converting more than 16% of the CO into CH_2O. CH_4 also was produced.

2786. Reichl, E. H. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, 128 pp.; PB 22,841; TOM Reel 200.

Contains information on location and production of 9 commercial Fischer-Tropsch plants in Germany; data on the supply and preparation of the Co catalyst; economic and operating data of large-scale commercial operations; development of the middle-pressure units; gas recycle operation; products from Fischer-Tropsch plants; adsorption of hydrocarbons on activated C; development work performed by the several organizations interested in the Fischer-Tropsch operations; the Synol process; synthesis of high-melting point waxes; isosynthesis; isobutanol synthesis; low-pressure MeOH synthesis; and the Oxo synthesis.

2787. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Location and Production of Commercial Fischer-Tropsch Plants in Germany. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 11–15; PB 22,841; TOM Reel 200.

Distribution of low-pressure and medium-pressure capacity among Fischer-Tropsch plants

German Fischer-Tropsch plants

(Based on actual production for 1942)

Operator	Location	Capacity		1,000 tons per mo. ave. mo. prod.				Low-pressure operation, tons per year	Medium-pressure operation, tons per year	Total tons per year
		Tons per year	Percent	Gasoline	Diesel fuel	Waxand kogasin	Lube oil			
Ruhrchemie	Oberhausen, Holten, Ruhr	72,000	12.0	2.1	0.8	1.4	1.2	18,088	44,545	62,633
Gewerkschaft "Viktor"	Castrop-Rauxel, Ruhr	40,000	6.8	1.5	1.0	.8	-------	37,699	-------	37,699
Rheinpreussen	Moers-Meerbeck, Ruhr	70,000	11.8	2.8	2.1	1.1	.2	67,212	-------	67,212
Krupp-Benzin[1]	Wanne-Eickel, Ruhr	60,000	10.2	2.2	1.1	1.7	-------	48,300	11,857	60,187
Hoesch-Benzin	Dortmund, Ruhr	47,000	7.9	.5	1.2	2.0	.2	-------	46,044	46,044
Braunkohle-Benzin	Ruhland, Saxony	170,000	29.2	8.4	2.5	3.1	-------	164,606	-------	164,606
Essener-Benzin	Bergkamen, Ruhr	80,000	13.6	4.1	1.8	.8	-------	79,974	-------	79,974
Schaffgotsch Benzin	Deschowitz, Silesia	40,000	6.8	.7	.8	1.8	-------	-------	26,374	26,374
Wintershall	Lutzkendorf, Saxony	[2] 70,000 12,000	1.7	.2	.1	.7	-------	11,468	-------	11,468
Total		591,000	100.0	22.5	11.4	13.4	1.6	427,377	128,820	556,197
Percent				46.1	23.3	27.4	3.2	76.8	23.2	100.0

[1] In this plant, the 1st stage operates at low pressure; the 2d stage at medium pressure.
[2] Under construction.

Product distribution of Fischer-Tropsch units, tons per year (1941)

Plant	Gasol	Gasoline	Kogasin	Diesel fuel	Paraffin (Gatsch)	Hard wax	Other products not sold directly	Total	Net sale value RM per year	Sale value pf. per kg.
Ruhrchemie	8,988	20,616	-------	8,454	-------	-------	14,855	52,913	13,504,550	25.40
Viktor	4,471	18,167	3,358	7,395	2,927	833	24	37,175	9,788,611	26.30
Rheinpreussen	7,379	34,191	6,656	16,394	5,093	1,408	-------	71,122	20,467,303	28.70
Krupp	4,657	25,531	-------	11,467	5,575	2,500	8,645	58,375	16,987,486	19.20
Hoesch	3,591	9,523	3,749	15,287	5,788	351	6,110	44,055	12,114,410	27.99
Brabag	8,421	77,955	-------	31,845	9,812	3,230	8,864	140,177	42,141,536	30.20
Essener	10,415	32,574	4,767	17,007	6,199	1,351	-------	72,312	20,677,082	28.50
Schaffgotsch	1,557	6,035	56	5,320	4,441	1,441	1,640	20,490	5,798,738	29.15
Wintershall	5	3,388	838	631	503	195	-------	5,561	1,685,762	30.31
Total	49,484	227,980	19,424	113,800	40,388	11,309	40,138	502,175	143,345,478	28.4 (ave.)
Percent	9.81	45.57	3.86	22.50	8.00	2.55	8.00	100.0		
Bbl. per day (7.5 lb. per gal.)	948	4,380	372	2,175	755	216	770	9,620		

License fee to Ruhrchemie was 1% of the net sales value of the products or 1,433,454 RM per yr. or 2.85 RM per ton.

Prices for different Fischer-Tropsch products were:

Gasol 22–26.6 pf. per kg.
Gasoline 25.7–31.5 pf. per kg.
Diesel oil 23.0–27.0 pf per kg.
Paraffin gatsch 20.5–25.0 pf. per kg.
Special waxes 56.0–92.0 pf. per kg.

2788. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Supply and Preparation of Cobalt Catalyst. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 15–18; PB 22,841; TOM Reel 200.

All existing plants were operated with the standard Ruhrchemie Co–ThO_2–MgO–kieselguhr (100:5:10:200) catalyst, which was supplied from 3 plants: Ruhrchemie (Ruhr); Brabag (Saxony); and Wintershall (Silesia), with respective capacities of 100, 65, and 35 oven fillings per mo., each roughly 1 ton. The overall Co consumption was 85–95 tons per yr., the loss in synthesis and in reworking being for Ruhrchemie 4.0 and 4.0%, respectively, and for Brabag 1.0 and 1.5%, respectively. The Co resources were barely enough to keep all plants running, Finland being the only source of supply. The method of preparation of the catalyst had not been changed since 1938 except for an improved drying apparatus, which not only dried the filter cake but shaped the catalyst with a minimum of abrasion loss in handling. It consisted of a drum, the outside surface of which was indented to form the molds, the filter cake being pressed on to it to give small (3-mm.) cylinders. The drum rotated slowly (0.1 r. p. m.), and hot gases passing through it dried the catalyst particles before they could reach the bottom, where having contracted slightly during drying, they dropped out by gravity. This method made it possible to use a softer kieselguhr, pretreated at 700° instead of 1,000°, which gave a more active catalyst.

2789. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Production Data From Commercial Large-Scale Operation. Cost of New Fischer-Tropsch Plants. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 18–21, 28; PB 22,841; TOM Reel 200.

Figures on the cost of Fischer synthesis plants according to Lurgi (basis 100,000 tons/yr.) are as follows: For a plant including the synthesis and recovery of products with the newest Fe catalyst using gas recycle and staging—400 RM/ton/yr./product; complete unit including gas generator—900 RM/ton/yr./product. According to I. G. Farbenindustrie (basis, 180,000 tons/yr.), for a plant including synthesis and recovery of products with Co catalyst and multiple stage operation without gas recycle—290 RM/ton/yr./product; complete unit including generator (coke basis)—590 RM/ton/yr./product; complete unit including conversion (natural-gas basis)—500 RM/ton/yr./product. On the basis of 100,000 tons/yr. the cost of the complete unit (coke basis) becomes 615 RM/ton/yr./product. Average monthly production data from the balance sheet of Brabag in 1943 are as follows:

(1) *Gas production:*
Total synthesis gas produced ...... 116,736,300 m^3 per mo.
CO+2 H_2 in gas 79%
Yield of gas from brown-coal briquets ...... 1,107 m^3 per ton

(2) *Synthesis:*
(*a*) Production: Kondensatoel ...... 6,306.1 tons per mo.—52%
Primary gasoline ...... 5,842.0 tons per mo.—48%
Liquid products:
Total ...... 12,148.1 tons per mo.—100%
Pure gasol ...... 2,836.7 tons per mo.—23.2%
Total ...... 14,989 tons per mo.
(*b*) Total yield per ton briquet ...... 157.2 kg.
(*c*) Total yield per m^3 gas ...... 128.4 gm.

(3) *Sales products* ...... 14,762.8 tons per mo.

(4) *Financial statement:*

(*a*) *Cost breakdown—material cost:*	*RM per ton prod.*
Briquets (at RM 9.60 per ton)	60.99
Outside coke (at RM 34 per ton)	20.15
Grude coke (at RM 23 per ton)	4.38
Raw coal (boilers) (at RM 2.4 per ton)	.92
Outside power (at pf. 1.9 per kw.-hr.)	4.04
Catalysts	9.61
Charcoal purification	1.20
Licenses	3.12
Total	104.41
Less credit for chemicals recovered	10.21
Net total materials cost	94.20

(*b*) *Other costs:*	*RM per ton prod.*
Hourly wages	46.80
Salaries	19.23
Other costs	42.10
Overhead	9.28
5% capital interest (basis 165,000,000 RM)	45.61
9% amortization (basis 149,000,000 RM)	74.12
Total operating expense	331.34
Sales	314.17
Loss	17.17

2790. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Medium-Pressure Fischer-Tropsch Units. 3-Stage Operation. Gas-Recycle Operation. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 23–27; PB 22, 841; TOM Reel 200.

In connection with the introduction of medium-pressure synthesis, it was found desirable to revise operations to produce liquid products with a maximum of olefins. The process used consisted in a combination of staging and gas recycle without substantial change in the operating temperature. It was found that considerable improvement could be made in the operation and the products by lowering the H_2 : CO ratio from the usual 2 : 1 to 1.94 : 1 then to 1.8 : 1 and 1.6 : 1. This resulted in improved liquid yields, higher olefin content, lower CH_4 formation, and higher average space velocity. The only apparent disadvantage was the decrease in the average catalyst life. Because of the low H_2 : CO ratio in the feed, a corresponding low ratio in the exit gas was obtained; therefore, since the ratio of consumption averages nearly 2.15 : 1, H_2 had to be added to convert the CO remaining from the first state in the second stage. To correct the ratio, H_2 in the form of converted water gas with a ratio of 3.79 : 1 was added. Even then the total conversion in the 2 stages was low. It was decided, therefore, to add a third stage, preceded by another addition of H_2. The favorable results of this operation with low H_2 : CO ratio led to adoption of the 3-stage operation in the 3 medium-pressure units at Hoesch, Ruhrchemie, and Lurgi. In spite of the general improvement in the operation, the olefin content of the products was still too low and finally was overcome by the use of gas recycle in the ratio of recycle gas to feed gas up to 3 : 1. The olefin content of the gasoline cut (200° end point) is about 70%, the Kogasin cut (200°–325°) about 45%. The temperature required to give adequate conversion is somewhat higher than in ordinary Co operation but does not exceed 225°, which can be reached with the existing steam-cooled reactors. The advantages derived from the above operation are: The shorter time required to bring the oven on stream; the increase in the yield per m^3 of synthesis gas. Thus in the first stage above, the same yield may be reached as before in 2 stages; higher space velocity with a corresponding decrease in the number of ovens required; lower catalyst cost; less disturbance to the operation from variations in the feed gas composition; higher olefin concentration in the products. In general the application of recycle lowers the boiling point of the product toward lighter materials, but this may be corrected by raising the CO : H_2 ratio.

2791. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Adsorption of Hydrocarbons on Activated Carbon. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 31–34; PB 22, 841; TOM Reel 200.

Process used for recovery of the gasol fraction from the products of the Fischer-Tropsch synthesis by means of activated C is described with reference to a diagram. In operation, at least 4 adsorbers are required, each chamber being used successively for adsorption, drying, and cooling. The desorption after adsorption is performed with steam. The C used, known as Supersorbon, is made from peat and activated by a $ZnCl_2$-steam treatment. The Lurgi Co. has developed a new C known as SK, which is activated with K_2S and is said to have about 2 times the capacity for low-boiling hydrocarbons as Supersorbon.

2792. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Development Work on the Fischer-Tropsch Process. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 35–69; PB 22, 841; TOM Reel 200.

Development work of Lurgi, Kaiser-Wilhelm Institute, Rheinpreussen, Ruhrchemie, Brabag, and I. G. Farbenindustrie on the Fischer-Tropsch process. Major attention was applied to the development of the Fe catalyst. Lurgi proposed 2 types of Fe catalysts: One precipitated on Si and operated at low temperature, 230°, designed to give a maximum of high-boiling-point product through polymerization; the second made from Lautmasse, a cheap product of the manufacture of Al from bauxite, impregnated with Cu and designed for the production of gasoline and olefins. Both operated with gas recycle; the product distribution of each was, respectively, gasoline 20 and 71%, Kogasin 20 and 20%, soft wax 15 and 9%, hard wax 45 and —%; the respective olefin content of the gasoline was 60 and 75% and of the Kogasin 45 and 60%. Kaiser Wilhelm Institute placed the research emphasis on the study of carbide formation in a precipitated Fe catalyst. Rheinpreussen likewise, and also on a catalyst based on Luxmasse with 0.15–5.0% K_2CO_3 and 0.0–3.0 Cu, which operated for 3.5 yr. and still gave 85% conversion at a space velocity of 80 and 113 gm. liquid product per m^3 of gas plus 32 gm. gasol. Ruhrchemie developed a precipitated Fe catalyst for wax production, which operated at low temperature, but an olefin producer did not get beyond laboratory stage. Brabag also developed Fe catalyst of the precipitated carrier type with emphasis on wax and olefin production, while I. G. Farbenindustrie studied the fused and sintered Fe (WK17) catalyst of NH_3 type and the effects of the reduction temperature, space velocity, and synthesis temperature on its productive capacity. Data of comparative tests of each of the above catalysts are presented. Reasonably good results were obtained from all. Attention also was paid to liquid-phase operation and 3 types of operation were tried: (*a*) Oel Kreislauf, the use of a solid catalyst bed with circulation of oil over the catalyst concurrently with the gas. It uses the fused Fe type NH_3 catalyst. The important features are the high space velocity, 200, and resulting high production from a given catalyst volume, 7.2 ton per 10 m^3. Olefin production is also high. The cost of a 100,000 ton per yr. plant is given as RM 57.2 per yr. per ton, as compared to RM 243 for the gas circulation process (I. F. Farbenindustrie), or RM 290 for a regular Fischer-Tropsch plant (Lurgi) with Fe catalyst and gas recycle. (*b*) Schaumfahrweise, suspension of the catalyst in the oil phase and dispersion of the catalyst with removal of the heat of reaction by circulating the slurry through an external cooler. Production of olefins and oxygenated products is high. (*c*) Static liquid phase, similar to (*b*), but the heat of reaction is removed by cooling tubes inserted in the liquid. This operation was regarded as highly promising. Some informtion is given concerning improvements in reactor designs, particularly the Krupp Taschenrohrofen at Wanne-Eickel, the Lurgi medium-pressure reactor, the I. G. Farbenindustrie medium-pressure reactor for the Synol plant, and the Rheinpreussen liquid-phase reactor.

2793. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. The Synol Process. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 72–92; PB 22,841; TOM Reel 200.

Development of the Synol process by I. G. Farbenindustrie is reported in detail. The process involves the direct synthesis of higher alcohols from CO and H_2 over a sintered Fe catalyst specially reduced by dry, pure H_2 at about 450° over a period of 50 hr. and medium pressure. The synthesis operation is performed at about 25 atm. and a temperature of 190°–225°. By raising the temperature, the same catalyst will produce a gasoline of 40–60% olefins with 65–75 octane number. With higher pressure, Fe carbonyl formation is considerable. The products consist almost wholly of straight-chain terminal alcohols, useful for making lubricating oils and detergents. Methods of separating the products are discussed at some length.

2794. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Isosynthesis. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 96–102; PB 22,841; TOM Reel 200.

Synthesis of low-boiling isoparaffins, as discovered in the laboratories of the Kaiser Wilhelm Institute, is a variation of the MeOH or the isobutyl synthesis. It operates at temperatures above those used in MeOH synthesis; although MeOH is believed to be an intermediate product. The upper temperature range is limited by the decomposition of CO at about 550°; this limit is constant for all pressures. The lower temperature limit is a function of the operating pressure; at 1,000 atm. the isosynthesis may be carried out at 400°; at 100 atm. a minimum of 450° is required. The kinetics of the synthesis is assumed to be as follows: (1) Formation of MeOH from CO and H_2; (2) dehydration of alcohol and immediate reaction with additional CO and H_2 to isobutylene and higher isoparaffins; (3) polymerization of isobutylene possibly followed by hydrogenation of alkylate, or formation of dimethylether from MeOH through addition of CO and H_2. At very high pressure the reaction proceeds as follows: $CH_3OH+CO+2\ H_2 \rightarrow CH_3OCH_3+H_2O$. The catalyst is pure ThO_2 or better combined with a dehydrating catalyst such as Al_2O_3; the % of Al_2O_3 based on ThO_2 varies 30–40%. A ThO_2–ZnO (1 : 1) catalyst does not give yields comparable to those with ThO_2–Al_2O_3; only 100 gm. per $m.^3$ as compared to 130 gm. per $m.^3$ The ThO_2 catalysts are virtually insensitive to S poisoning and their long life is remarkable. The synthesis is carried out in a single pass with the feed gas containing CO–H_2 in the ratio 1 : 1.2; 70–75% conversion is obtained at average space velocities of about 1,350, 150 atm., and 450°. The products obtained are mostly low-boiling isoparaffins with isobutane the largest individual component.

2795. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Isobutanol Synthesis. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 103–108; PB 22,841; TOM Reel 200.

Isobutanol synthesis was a prewar I. G. Farbenindustrie development and was practiced for the production of isobutylene polymer (Oppanol) and isooctane. The high-boiling fractions were useful for production of detergents and lubricants. The isobutanol synthesis uses the same raw materials as the MeOH synthesis, virtually the same catalyst, and like pressures, about 240 atm. The catalyst in ZnO–Cr_2O_3–KOH (60 : 40 : 1 parts). The temperature used is about 430°. Compared with the MeOH synthesis, the output per catalyst volume is low since the main product MeOH is recycled to extinction; about 5–6 parts of MeOH are obtained for each part of isobutanol. The higher alcohols and ketones make up about 15% of the total product. An important part of the isoBuOH synthesis, which increases the yield of isoBuOH and utilizes one of the byproducts, is the reaction of isobutyron (diisopropyl ketone) with CH_2O to give 2 mol. of isoBuOH. A detailed list of the compounds contained in the product is given to illustrate the complexity of the composition. Separation of the products from the synthesis is by fractional distillation.

2796. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. Low-Pressure Methanol Synthesis. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 109–113; PB 22,841; TOM Reel 200.

This synthesis of MeOH is carried out at 30 atm., compared with usual operation at 250 atm. The work had been carried out on a laboratory scale and a pilot plant had been built. The process is as follows: A solution of Na metal in MeOH, 5.8 gm. in 100 gm., is charged to an autoclave and a pressure of 30 atm. set up by feeding CO. The temperature is maintained at 80°. The crude product, a mixture of MeOH and CH_3COOH, is separated from the catalyst salts by distillation and is then hydrogenated over a catalyst of Cu–Cr–Ba oxides at 175°–185°. The products of hydrogenation are separated by fractional distillation. Overall yields of 95% to MeOH are claimed.

2797. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. The Oxo Synthesis. U. S. Naval Tech. Mission in Europe Rept. 248–45, 1945, pp. 114–128; PB 22,841; TOM Reel 200.

Oxo synthesis is a process for the production of alcohols by the action of olefins with 1 mol. each of CO and H_2 and subsequent hydrogenation of the resulting aldehyde. The process was developed by Ruhrchemie and I. G. Farbenindustrie and a plant was built at Holten but never operated. The information in this report is based on large-scale pilot-plant operation and laboratory work. The chemistry of the process was studied, and pure olefins of different types were subjected to the Oxo reaction and the products separated and analyzed. The compounds charged to the Oxo synthesis are known to be substantially terminal olefins, yet it was found that some of the products could have been formed only if a double bond shift had preceded the formation of the aldehyde. Tests with *n*–dodecylene–1 proved that from terminal normal olefins the Oxo synthesis yields branched alcohols, particularly 2–alkyl alcohols, whereby the yield decreases with increasing length of the sidechain. It was finally possible to prove that Co carbonyl was the catalyst responsible for the double bond shift. Fe carbonyl showed a similar effect but not the same activity, and Ni had no effect at all. Many materials were tested as feed for the synthesis; it appears that the reaction is applicable in principle to all monoolefins independent of origin, although synthetic olefins are preferred because of their higher purity. Compounds containing double bonds give unsatisfactory results. The customary catalyst is the CO–ThO_2–kieselguhr (100 : 1.5 : 200) applied as a slurry in the liquid feed in concentration of 3% by weight of the olefins. It does not contain MgO, because this encourages condensation of the aldehydes. One of the main problems in the process, as noted above, is the formation of Co carbonyl. The I. G. Farbenindustrie developed a Co–Cu catalyst that gave only a fraction of the carbonyl and was satisfactory for the first stage (aldehyde formation) but did not hydrogenate well. The catalyst is recovered from the reactants at the end of the operation by filtration and returned for further use. In a modification of the process, Co acetate is contacted with fatty acids in an autoclave to yield the Co salt, and this is introduced in solution into the feed to give a concentration of 0.02–0.05% of Co. This mixture is charged to the reactor where it passes over a solid Co catalyst bed (Co on pumice) and is finally freed from the Co in a special smaller reactor filled with plain pumice by being reduced with H_2 and deposited on the pumice. This reactor is purged of Co after several months by forming the carbonyl, which is again dissolved in oil and returned to the feed. The operating conditions for both the batch and the continuous processes and the fractionation of the products are described. The over-all cost of the final product is given as 0.60–0.65 RM per kg. of alcohol. Further development of the process probably will be toward continuous operation and better control of the synthesis, particularly the suppression or close control of the double bond shift to give clearly defined α-substituted alcohols of predetermined branching.

2798. ———. Synthesis of Hydrocarbons and Chemicals From Carbon Monoxide and Hydrogen. BIOS Misc. Report 60, 1947, 128 pp.; PB 22,841.

This report is a reproduction of United States Naval Technical Mission in Europe Rept. 248–45, PB 22,841. It covers the Fischer-Tropsch process, the Synol process, synthesis of high melting point waxes, isosynthesis, isobutanol synthesis, low pressure MeOH synthesis, and the Oxo synthesis.

———. *See* abs. 1469.

2799. Reid, J. B. Recovery of Byproducts in High-Temperature Coking. British Coal Utilisation Research Assoc., Monthly Bull., vol. 9, No. 8, 1945, pp. 225–234.

Review with 46 refs. Reformation of coke-oven gas is directed principally to producing mixtures for hydrocarbon synthesis. The various reactions by which CH_4 can be converted are:

(1) $CH_4=C+2H_2-18$ kcal.
(2) CH_4+H_2O (vapor) $=CO+3H_2-49.5$ kcal.
(3) $CH_4+CO_2=2CO+2H_2-59.5$ kcal.
(4) $CH_4+\frac{1}{2}O_2=CO+2H_2+8.5$ kcal.

All the reactions require temperatures of about 1,200° C; at a lower temperature reaction (2) merges into the exothermic reaction: $CH_4+2H_2O=CO_2+4H_2$. 5 reformation processes, based on the above reactions and directed principally to producing gas mixtures of composition CO : H_2=1 : 2, have been developed: The Fischer process in which the CH_4-containing gas is passed with steam through coke in a water-gas generator, producing mixtures of H_2 and CO in the ratio of 2 : 1 when suitable adjustment is made of the gas : steam ratio and the lengths of gas and blow periods; the Linde process makes use of reaction (4) by which it is claimed that 90–95% of the CH_4 is converted giving a final gas mixture very near to $2H_2+CO$; the Kuhlmann process operates reaction (2) at hot inert surfaces, the gas and steam being the sole reactants, the resulting gas mixture being mainly H_2 and CO in the ratio of 4 : 1; the Koppers process, which is similar to Kuhlmann, in that it makes use of thermal reformation at hot surfaces with an efficiency of 90–95% as against 75% for the Kuhlmann process; the I. G. Farbenindustrie process is catalytic and is conducted at about 800° C. on a Ni catalyst, it depends on reactions (2) and (3) so that both CO_2 and steam are added to the gas mixture, and the product is H_2 and CO in a ratio of almost exactly 2 : 1.

2800. Reinäcker, G. [Heterogeneous Catalysis and Atomic Structure.] Die Chemie, vol. 57, 1944, pp. 85–90; Chem. Abs., vol. 40, 1946, p. 4593.

Discussion with 76 refs. The magnetocatalytic effects of Ni-Fe catalysts on the decomposition and hydrogenation of CO are of interest in connection with the change in catalytic activity above the Curie-point temperature. The change in activity that occurs at the Curie point is due to electronic changes.

2801. Reinders, W. [Composition of Water Gas at Lower Temperatures.] Ztschr. physik. Chem., vol.

130, 1927, pp. 405–414; Chem. Abs., vol. 22, 1928, p. 860.

Mathematical treatment of the various equilibria among the components of water gas is given with a discussion of the Fischer synthesis of hydrocarbons from CO and H_2 and a probable explanation of the formation of CH_4.

Reinhard, O. *See* abs. 3245.

Reinov, N. *See* abs. 65.

2802. Reis, T. [Theoretical and Experimental Contributions to the Study of Fluid Catalyst Systems.] Bull. assoc. franç. techniciens pétrole, No. 76, 1949, pp. 3–44; U. O. P. Co. Lib. Bull., Oct. 5, 1949.

This article is composed of 3 parts. The 1st part discusses the theory of fluid catalysis and reviews the work of other investigators. Semiempirical formulas are introduced for making the following calculations: (*a*) The length of time the particles are in a reactor; (*b*) the loss of charge; (*c*) the distinction between aggregative and particulate fluidization; (*d*) the initial expansion of the solid particle bed; (*e*) the efficacy of fluidization; (*f*) the loss of charge in the case of horizontal or vertical flow of the dispersed suspensions. The 2d part describes a new experimental method for directly controlling the behavior of dispersed catalyst suspensions. The 3d part is devoted to new theoretical conceptions of fluidized systems.

Reisemann, E. *See* abs. 137.

2803. Reisinger, —. Report on the Synol Synthesis. TOM Reel 134, Rept. 283, May 2, 1941, 19 pp.

In the examination of catalysts for the reaction, the fused Fe catalyst WK17, Leuna NH_3 catalyst, gave the best results; the Oxo fraction, 230°–350°, of the primary products contained 25–35%, by weight, of alcohols. Fe precipitation catalysts with promoters were tried. The most active of these was the Fe–Al type, which, with a specific total yield of 84.3 gm. per N m.^{3}, gave 42.5% alcohol by weight, in the Oxo fraction. Also worthy of note are the catalysts Fe–Mn and Fe–Ni. The amount of promoter element should not exceed 1–3% for the best results. Experiments on the influence of temperature on the course of the synthesis showed that a maximum alcohol yield only can be obtained at low temperatures, 200°–240°, and with low gas conversions, 40% contraction. The chemical natures of the Fe catalyst primary products were determined by fractional distillation. The alcohol concentrations were found to increase with rising temperature continuously up to a maximum at 100°–180°, C_4–C_7, with a concentration of 30% alcohol, then decrease fast to 11%, rising again to a maximum at 300°–320°, approximately C_{15}. At still higher temperatures, virtually no alcohols were present. During distillation of the primary product, the acids contained in the product esterify corresponding amounts of alcohol. By deacidification of the products before the distillation starts, the alcohol contents in the fractions above 200° can be retained. A comparison is given on the composition of products obtained by the 2 methods. By heating the high-melting paraffins, 84° and more in air, varnishlike coatings of good qualities have been obtained.

2803a. Reitlinger, O. [Increasing the Efficiency of Catalysts for Gas Reactions.] Chem. Ing.-Tech., vol. 24, 1952, pp. 1–2; Chem. Abs., vol. 46, 1952, p. 3,681.

Catalysts are prepared by depositing powdered active catalytic materials on catalyst carrier by means of hydrated bonds. Preparation of an Fe_2O_3 catalyst is described in detail and data are presented for 6 examples as follows: Chlorination of CH_4 and C_2H_4, $C_2H_4+HCl \rightarrow C_2H_5Cl$, $C_2H_2+HCl \rightarrow C_2H_3Cl$, $2C_2H_2+3H_2O \rightarrow CH_3COCH_3+2H_2+CO_2$, and hydrogenation of CO.

2804. Reitmeier, R. E., Atwood, K., Bennett, H. A., and Baugh, H. M. Production of Synthesis Gas by Reacting Light Hydrocarbons With Steam and Carbon Dioxide. Ind. Eng. Chem., vol. 40, 1948, pp. 620–626; Chem. Abs., vol. 42, 1948, p. 4328.

Study was made by the Girdler Corp. to establish the optimum conditions for the production of synthesis gas mixtures for the Fischer-Tropsch reaction, having a ratio of H_2 : CO capable of being varied between 0.5 and 3 in the same equipment without running into difficulties brought about by the deposition of C, by controlling the temperature and the composition of the reactant. This study involved consideration of the equilibria when light hydrocarbons are reacted with steam and CO_2 and attempted to predict the conditions necessary to prevent C deposition. Calculation of the proper proportion of reactants to be introduced into the furnace for the production of the desired ratio was included. Following this, laboratory-scale experimental work was conducted to determine the possibility of approaching the conditions predicted. Finally the work was expanded to pilot-plant scale as a successful result of which a plant is being constructed at Bruceton for the Bureau of Mines. The paper presents curves and formulas that have been developed to facilitate the selection of conditions and reaction mixtures of light hydrocarbons, steam, and/or CO_2 to produce a synthesis gas having a wide range of compositions. Laboratory experimental data are given, which demonstrate that the conditions and compositions predicted by the curves can be closely approached in actual practice. Pilot-plant investigations also are described, which show that the process is commercially feasible.

Reitstoetter, J. *See* abs. 3588.

2805. Rembashevskii, A. G. [Enriching of Binary Gas Mixtures.] Trudy Leningrad. Khim. Tekhnol. Inst., No. 6, 1938, pp. 288–312; Khim. Referat. Zhur., vol. 1, No. 8–9, 1938, pp. 3–4; Chem. Abs., vol. 33, 1939, p. 9593.

Artificially prepared mixtures of CO and H_2 were passed through a layer of the cataylst [Ni obtained from $Ni(NO_3)_2$] at 200°, 240°, 280°, and 320°. For CO : H_2=1 : 3, the reaction $CO+3H_2 \rightleftharpoons CH_4+H_2O$ reaches its maximum at 280° (92.8% CH_4, 8% H_2). The 1 : 1 and 1 : 2 mixtures yield less CH_4, and C is deposited from the side reaction $2CO \rightleftharpoons CO_2+C$. No advantages were obtained from the substitution of Co for Ni. The maximum CH_4 formation took place at a higher temperature. The use of Fe–Zn, and of a specially prepared Fe catalyst gave unsatisfactory results. To obtain the CO : H_2= 1 : 3 binary gas mixture, half of the gas, free from H_2S and from CO_2, was passed at 450°–500° through a converter, Fe oxide with the oxides of Cr, Mg and other metals as catalysts. The CO is oxidized by water vapor according to $CO+H_2O \rightleftharpoons CO_2+H_2+10{,}000$ kcal. After removing the CO_2, both gases are mixed, dried, and passed over the catalyst. Experiment with binary peat gases gave a product with a 4,500 kcal. heat capacity, and an 80.43% yield. Analogous results were obtained from the 1 : 1 mixtures, but the 1 : 3 mixture reaction was faster, and it took place at a lower temperature. The best catalyst was Ni–Al_2O_3 (stable to contact contamination). Prepared water gas was passed through the catalyst at 250°–280° with an increasing velocity until the heat capacity of the final product was below 4,000 kcal./m.^{3}. The reaction yield increased with the velocity and decreased with the increase of the heat capacity of the final product. A temperature increase, in the 250°–280° region, for the same heat capacity of the final product caused a decrease of the yield and an increase of the velocity. It was calculated that a 100,000 m.^{3}/hr. enriching of the gases to 3,000, 3,600, 4,500, and 5,800 kcal./m.^{3} is commercially profitable only if the products are used close to the production plant.

Remeika, J. P. *See* abs. 1136.

2806. Rennekamp, F. [Composition of Fat Acids in a Fat Obtained From Oxidation Products of Synthetic Paraffin.] Ztschr. physiol. Chem., vol. 259, 1939, pp. 235–244; Chem Zentralb., 1939, II, p. 3061; Chem. Abs., vol. 33, 1939, p. 7605.

Synthetic fat contained all the fat acids from C_8 to C_{22} with about equal quantities of odd and even numbers of C atoms. It melts at 27°–29°, has I No. 4.2, acid No. O, saponification No. 231, and unsaponifiable 0.3%. The Me esters were fractionated and some of the acids isolated pure from the fractions.

2807. Renzi, E. [Industrial Utilization of Methane.] Atti III° convegno naz. metano, vol. 2, 1941, pp. 293–296; Chem. Zentralb., 1942, II, p. 1989; Chem. Abs., vol. 38, 1944, p. 3108.

Applications discussed are: Decomposition of CH_4 above 900° with catalysts into H_2 and lampblack, and utilization of the lampblack for making printer's ink, etc.; decomposition of the H_2, for example, for synthesizing NH_3 or liquid motor fuels; transformation of CH_4 and H_2O vapor at 900° with Ni catalyst to CO_2 and H_2; transformation of CO_2 in gas producers according to $C+CO_2=2\ CO-37$ cal.; use of the CO and H_2 for the synthesis of hydrocarbons or MeOH; preparation of a mixture of C_2H_4, C_2H_2 and H_2 by treatment of CH_4 with a spark discharge; transformation of the mixture at 200°–250° at normal pressure with Ni catalyst into benzine.

2808. Reppe, —. New Syntheses of Acrylic Acid. Modern Plastics, vol. 23, No. 3, 1945, pp. 162–165, 210; Chem. Abs., vol. 40, 1946, p. 1449.

Translation of a captured German report by the above author, obtained under auspices of U. S. War Department. Metal carbonyls promote reaction between C_2H_2 or olefins, CO and H_2O, alcohols, or other compounds containing labile H. Cyclopropenones or cyclopropanones probably form as intermediates by interaction between C_2H_2 or olefin and CO. These intermediates hydrolyze or alcoholyze to the corresponding acids or esters. Acrylic esters or amides are obtained from C_2H_2, CO, and alcohol or amine with Ni and NiI_2 catalyst at 150°. Similarly, olefins with CO and alcohols give almost quantitative yields of saturated carboxylic acid esters. α–olefins yield a mixture of straight chain and α–Me substituted acid esters. The Oxo synthesis of aldehydes also is explained as owing to hydrogenolysis of a cyclopropanone intermediate. $Ni(CO)_4$ (0.25 mol.) added dropwise to a mixture of EtOH (1 mol.) and concentrated HCl (0.5 mol.) saturated with C_2H_2 gives $CH_2 : CHCO_2Et$ virtually quantitatively. Similarly other alcohols give the corresponding acrylate esters, mercaptans give acrylic thio esters, amines give acrylic amides, and H_2O gives $CH_2 : CHCO_2H$, all yields being substantially quantitative. Co carbonoyl, but not Fe carbonyl, may replace $Ni(CO)_4$ in this reaction. $NiCl_2$ solution resulting from the process is reclaimed by adding NH_3 in slight excess over the requirement to form $NiCl_2$ hexamine and treating with CO at 80° and 50–100 atm. to form $Ni(CO)_4$.

Rescorla, A. R. *See* abs. 3082.

2809. Research Council of Alberta. Fischer-Tropsch Synthesis of Liquid Fuels. Annual Rept. 45, 1944.

In 1944 a project was begun concerned with the improvement and development of catalysts. Equipment was designed, erected, and tested to provide for water gas production and a battery of 6 catalyst testers. A start had been made on catalyst preparation, and it was expected that all equipment, testing and control methods, operating technique, and procedures would be completed and runs started by March 1945.

2810. ———. Natural-Gas Research. Annual Director's Rept. 47, 1945, pp. 14–15.

Study of the Fischer-Tropsch synthesis of gasoline and other liquid fuels was begun in 1944 (abs. 2809) in cooperation with the Federal Bureau of Mines. The process is of interest as a possible source of liquid fuels from natural gas or coal since Alberta has large reserves of both of these natural resources. The work thus far is concerned mainly with a study of catalysts, and early in 1945 some static tests were carried out, the results of which are to be correlated with continuous tests now under way.

2811. Rettenmaier, A. [Process and Raw Materials for Complete Gasification of Coal and Its Importance in Meeting Further Increased Gas Demands.] Gas- u. Wasserfach, vol. 84, 1941, pp. 473–477; Chem. Abs., vol. 36, 1942, p. 5333.

Development of processes for the complete gasification of lignite is reviewed. 2 new processes have been developed for the gasification of bituminous coals by means of O_2 and steam, 1 using pulverized coal and the other, the Thyssen-Galocsy process, using lump coal. The latter process, described, gasifies noncoking coals in a shaft generator from which the slag is removed in molten form. The section of the generator resembles that of a blast furnace. To avoid hot spots in the combustion zone, a portion of the injected O_2 is mixed in a small precombustion chamber with some of the process gas or other suitable gas. Decomposition of the added steam is virtually complete at the high temperature employed. The resulting oxygas can be used for synthesis purposes or methanized to town gas. The technical problem of methanization using a Ni catalyst is now claimed to be solved. The efficiency of the Thyssen-Galocsy generator, including gas and tar, is about 90%, or, taking into account the energy required for the O_2 used, about 80%. Costs given.

2812. Revue pétrolifère. [Substitute Motor Fuels, A Study of Hydrogenation Processes From the Economic Standpoint.] Feb. 8, 1930, p. 210.

Yields per ton of coal treated are given for various processes. The Bergius process yields 150 kg. of gasoline, 200 kg. of diesel or impregnating oil, 80 kg. of fuel oil, and 60 kg. of lubricating oil. The Patart, Badische Anilin u. Soda Fabrik, or Fischer-Tropsch methods give 400–600 kg. of MeOH, 200–600 kg. of liquid hydrocarbons, and recovery of the gases from coke manufacture, 5–10 kg. of C_6H_6, 5 kg. of EtOH, 5–7 kg. of MeOH. The Fischer process at ordinary temperature requires a very large plant. The apparatus for the production of synthetic MeOH, although less cumbersome, is not less costly.

Reyerson, L. H. *See* abs. 2328.

Reynolds, D. A. *See* abs. 3213, 3214.

2813. Rhead, T. F. E., and Wheeler, R. V. Effect of Temperature on the Equilibrium $2\ CO \rightleftharpoons CO_2+C$. Proc. Chem. Soc., vol. 26, 1910, p. 220; Jour. Chem. Soc., vol. 97, 1910, pp. 2178–2189; Chem. Abs., vol. 5, 1911, p. 641.

In an electric furnace constructed so that a given temperature could be maintained, without serious fluctuations, for several weeks, and with a N_2 jacket around the reaction tube to prevent diffusion of O_2, pure CO_2 was circulated over pure wood charcoal until the pressure became constant. The values obtained for the equilibrium are as follows: At 850°, by vol., 6.23% CO_2 and 93.77% CO; 900°, 2.22, 97.78; 950°, 1.32, 98.68; 1,000°, 0.59, 99.41; 1,050°, 0.37, 99.63; 1,100°, 0.15, 99.85; 1,200°, 0.06, 99.94. By means of the equation $(19{,}500/T)+\log_e C_1^2\ \log_e C_2=k$ (from LeChatelier's equation for the equilibrium in gaseous systems), the following values for k, at the above series of temperatures were calculated: 20.01, 20.39, 20.24, 20.44, 20.32, 20.70, and 20.65. At 850°, the speed of reduction of CO_2 by C was found to be 116 times that of the reverse reaction. (*See* abs. 185, 319, 698, and 3068.)

2814. ———. Effect of Temperature and Pressure on the Equilibrium: $2\ CO=CO_2+C$. Jour Chem. Soc., vol. 99, 1911, pp. 1140–1153; Chem. Abs., vol. 5, 1911, p. 3644.

Authors have previously investigated this equilibrium at atmospheric pressure (abs. 2813). Further measurements have now been made at 0.5–3 atm., in order to prove whether the expression $(N'-N)\ \ln P$ in Le Chatelier's general equation for mobile equilibrium satisfies experiment in this particular case. The reaction vessel of quartz glass was heated in an electric resistance furnace wound with Pt wire. Temperatures ranged from 800°–1,100° and were measured by means of a Pt–PtRh thermocouple placed outside the quartz vessel. The equation $(38{,}055+2.02\ T-00031\ T_2)2\ T+\ln P+\ln\ (C_1^2/C_2)=k$ was found to satisfy the data obtained. In this equation T is absolute temperature, P the pressure in atmosphere, C_1 and C_2 the fractional concentrates of CO and CO_2, respectively, and k a constant. Equilibrium was reached rapidly at the higher temperatures, but at 800° it was attained only after heating for more than 70 hr.

Rheinheimer, W. *See* abs. 1610.

Ri, T. *See* abs. 1489.

2815. Rice, F. O. Attempts to Prepare the Methylene Radical by the Thermal Decomposition of Hydrocarbons. Jour. Am. Chem. Soc., vol. 61, 1939, p. 213; Chem. Abs., vol. 33, 1939, p. 1663.

Results indicate that trivalent C radicals are the primary products of organic dissociations, and even in the few cases, such as CH_2N_2 and $CH_2:CO$, in which CH_2 is the primary product, it passes readily into the trivalent state.

2816. Richards, T. W., and Davis, H. S. Heats of Combustion of Benzene, Toluene, Aliphatic Alcohols, Cyclohexanol, and Other Carbon Compounds. Jour. Am. Chem. Soc., vol. 42, 1920, pp. 1599–1617.

Heat of combustion of MeOH in 18°-cal. per gm. was found to be 5,326.

2817. Richardson, R. E., and Others. Synthetic Emulsifying Agents, Wetting Agents, Detergents, and Soap Substitutes. PB 6,684, 1945, 38 pp.

Trade names, chemical composition, and manufacturing process for the products made by I. G. Farbenindustrie A.-G. Among the products mentioned are: Igepons and Igepals, alkyl–aryl–sulfonate-type detergents, made from Fischer-Tropsch oils, and Mersol emulsifiers.

Richardt, F. *See* abs. 1299.

Richter, H. *See* abs. 1832, 1833.

Richter, M. *See* abs. 3089.

2818. Rideal, E. K. Note on a Simple Molecule Mechanism for Heterogeneous Catalytic Reaction. Proc. Cambridge Phil. Soc., vol. 35, 1939, pp. 130–132.

Proposed mechanism involves 2 assumptions: (1) That surface catalytic reactions take place between a chemisorbed radical or atom and a molecule derived from the gas phase; (2) that in the interaction between the 2 species the covalent bond between the chemisorbed constituent and substrate either is not broken or is converted into the van der Waals bond.

2819. ———. Mechanism of Catalytic Hydrogenation. Chem. and Ind., 1943, pp. 335–338; Chem. Abs., vol. 38, 1944, p. 15.

An address on the development and extension of Sabatier's ideas by Rideal over the last 20 yr. is given. In agreement with Sabatier, and contrary to the views of H. S. Taylor, Rideal concludes that a metallic catalyst is covered with a monolayer of chemisorbed H_2, which is adsorbed without appreciable energy of activation. Further changes in H_2 retention with temperature are due to solution of H_2 in the metal, or activated diffusion. The methods of photoelectric thresholds, or better, the change in contact potential caused by the presence of a monolayer were used by Rideal to study the chemisorbed layer. The ortho-para H_2 conversion at a metallic surface is due to interaction between a chemisorbed and a van der Waals adsorbed species and, thus, can be used as an indicator for chemisorbed H atoms. This is an aid in explaining the mechanism of certain hydrogenation reactions. The theory of intermediate compound formation best explains such hydrocarbon catalysis reactions as the exchange of H and D in C_2H_4 and C_2H_6, and the migration of the double bond in higher olefins under conditions when exchange occurs. Although the mechanism by which H_2 is added across a double bond at the surface of Ni is as yet uncertain, present evidence favors the view that catalytic hydrogenation proceeds through the addition in 1 step of an undissociated molecule of H_2. Organometallic intermediate compounds explain also the catalytic cyclization reactions of heptane, octane, and the Fischer-Tropsch synthesis. The main reactions occurring in the latter are due to van der Waals adsorbed H_2 alone rather than chemisorbed H_2, which in this synthesis causes formation of large quantities of CH_4.

———. *See* abs. 643, 808, 1407, 1519, 1520, 3510.

2820. Rideal, E. K., and Trapnell, B. M. W. [Adsorption of Hydrogen by Tungsten, and the Mechanism of Para-Hydrogen Conversion at Tungsten Surfaces.] Jour. chim. phys., vol. 47, 1950, pp. 126–138; Chem. Abs., vol. 44, 1950, p. 7118.

The adsorption of H_2 was measured over the temperature range −185° to 0° and pressure range 1.5×10^{-7} to 10^{-2} mm. on a film of W formed by evaporation of W atoms from a wire. The equilibrium adsorption changed very slowly with temperature and pressure, increasing only 9% at 0° for a 10^4 pressure increase and only 14% on dropping the temperature from 0° to −183° at 10^{-2} mm. If the surface area of the film is judged from the chemisorption of O_2, the measurement represents coverages in the range 60%–90%. The heats of adsorption calculated by the Clausius Clapeyron equations are 14, 11, 7, 3, and 2 kcal. per mole at coverages of 70, 75, 80, 85 and 90%, respectively. The data fit a Freundlich isotherm. Quantitative analysis of the data leads to the conclusion that the observed fall in heat of adsorption with coverage cannot be accounted for on the basis of simple electrostatic dipole-dipole repulsions. The data are consistent with the rate of interconversion of ortho-para H_2 observed by Eley and Rideal (abs. 808) if it is assumed that this reaction is the result of alternate chemisorption and evaporation of H_2 mol. from a surface that is so extensively covered with H_2 as to have a low heat of desorption of H_2 mol.

2821. Riedel, H. G. [Status of Scientific Knowledge and Technical Development in the Field of Tar Processing, Extraction and Synthesis.] Bergbau-u. Energiewirtsch., vol. 2, 1949, pp. 243–250; Chem. Zentralb., 1950, II, p. 1765.

Subjects discussed are: Preparation of low-temperature tars, their processing, extraction, and hydrogenation, and the Fischer-Tropsch process.

2822. Riedl, R. [Gas Developments in Czechoslovakia.] Rev. gén. gaz, vol. 69, No. 3, p. 73; Coke and Gas, vol. 9, 1947, p. 350.

Summary of a detailed study of the production of gas by the Lurgi process and of the development of the Czech gas industry within the 2-year plan provided by nationalization. Typical analyses are given of gas

obtained by treatment of a Czech lignite. A Lurgi producer, dealing with 8–20 mm. lignite and rate at 3,000–4,000 m.³ of gas/hr., produced 700 m.³ of gas and 80 kg. of tar/metric ton of lignite and requires/m.³ of gas: O_2, 0.19 m.³ at 22 atm.; steam, 1.25 kg. at 25 atm.; electric energy, 0.16 kw.-hr.; and water 0.06 m.³ Three Lurgi producers at the Stalin works near Möst have been in service since 1945 and appear to have given no difficulty in operation. A map shows the development of the Czech gas industry.

2823. ———. [Manufacture of Synthetic Liquid Fuels.] Paliva a voda, vol. 27, May 20, 1947, p. 74; Fuel Abs., vol. 2, No. 3, 1947, p. 41; Chem. Abs., vol. 42, 1948, p. 5199.

The author stresses the interest for the manufacture of artificial motor fuel even in those countries that possess their own naphtha sources. Two basic manufacturing methods, Fischer-Tropsch and Bergius, and a schematic manufacturing method at the Stalin works are described.

Riedler, G. *See* abs. 3578.

Riehl, N. *See* abs. 1234.

Ries, H. E. *See* abs. 1625a.

Riesz, C. H. *See* abs. 1957, 1958, 1959.

2824. Riesz, C. H., Lister, F., Smith, L. G., and Komarewsky, V. I. Catalysts for Hydrocarbon Synthesis. Ind. Eng. Chem., vol. 40, 1948, pp. 718–722; Chem. Abs., vol. 42, 1948, p. 4325.

Hydrocarbon synthesis catalysts are regarded as complex-action catalysts, combining hydrogenation and polymerization. Although complicated by carrier and promoter effects, the above was substantiated by preparation of 2-component catalysts containing Co, Ni, or Fe for the hydrogenating action; ThO_2, SiO_2, Al_2O_3, or ZnO as polymerization components. Co–ThO_2, Co–SiO_2, and Co–Al_2O_3 were particularly active catalysts, optimum liquid formation occurring when the metal content of the catalyst was 75% by weight. Ni catalysts formed excessive amounts of gaseous hydrocarbons, but Fe catalysts were relatively inactive in the absence of elevated pressure.

Rigamonti, R. *See* abs. 2395, 2396, 2397.

2825. Rikles, B. [Liquid and Solid Hydrocarbons From Natural Gas—the Fischer-Tropsch Process in Argentina.] Bol. inst. sudamer. petrol. (Montevideo), vol. 2, 1947, pp. 543–593; British Abs., 1949, B, I, p. 37.

Review with 88 refs.

2826. Riley, H. L. (Chairman). Chemicals From Coal in the North of England. Coal-Processing Industries Report. Chem. Age, vol. 53, 1945, pp. 565–568.

Objectives to be considered are the development of the tar distillation industry and the extraction of C_2H_4 from coke-oven gas. The statement is made that the Northeast provides one of the most suitable areas in the country for large-scale trials of the Fischer-Tropsch process. The County of Durham, with its large coke-producing units and potential reservoirs of surplus gas, is eminently well-placed for this research work, and the products made by the Fischer-Tropsch process may be linked with those from the C_2H_4 extraction plan.

2827. ———. Carbides, Nitrides, and Carbonitrides of Iron. Quart. Revs. (London), vol. 3, 1949, pp. 160–172; Chem. Abs., vol. 43, 1949, p. 7361.

Review with 64 refs.

Riott, J. P. *See* abs. 2881.

2828. Risenfeld, E. H. [Significance of the Fischer Synthesis (Hydrogenation of Carbon Monoxide) in the Domestic Manufacture of Benzene and Lubricating Oil in Sweden.] Tek. Tid., vol. 66, Uppl. A–C, Kemi, 1936, pp. 89–98; Chem. Abs., vol. 31, 1937, p. 3665.

Fischer-synthesis process, in contrast with the Bergström and the Bergius processes, offers the only possibility for the production of liquid hydrocarbons in Sweden, for which only wood, peat, or charcoal is available as the raw material.

Ritchie, A. W. *See* abs. 179, 180.

2829. Ritman, E. L. Carbohydrates and Related Constituents of Plant Tissues as a Supplement to Coal and Petroleum. Trans. World Power Conf., Fuel Conf., Sec. A–3, Paper 8, 1947, 7 pp.; Chem. Abs., vol. 42, 1948, p. 736.

Best method of converting carbohydrates and related constituents of plant tissues to fuel appears to be the fermentation of a suspension containing dissolved carbohydrates. It is probable that 3 m.³ or more pure CH_4, mixed with CO_2 in ratio of about 7 CH_4 : 3 CO_2, can be produced per 24 hr. per m.³ of tank vol. The gas mixture is very suitable for the Fischer-Tropsch synthesis.

Ritter, H. *See* abs. 1206.

2830. Rivett, D. Oil Production From Coal From an Australian Viewpoint. Petrol. Times, vol. 38, 1937, pp. 629–633; Engineering, vol. 144, 1937, pp. 748–749; Iron and Coal Trades Rev., vol. 136, 1938, pp. 653–654; Brennstoff-u. Wärmewirt., vol. 20, 1938, pp. 87–92; British Chem. Abs., 1938, B, p. 129.

Economic possibilities of establishing, in Australia, plants for producing gasoline from coal by direct hydrogenation or by the Fischer process have been investigated by a Government committee. The scheme was received unfavorably.

2831. Robell, J., and Dewling, W. L. E. Methanol Synthesis at the I. G. Farbenindustrie A.-G. Plant at Oppau; FIAT Rept. 888, 1946, 14 pp.; PB 47,864; TOM Reel 240.

Presents information on process and equipment design of the MeOH synthesis plant at Oppau, and reviews the latest developments achieved by I. G. Farbenindustrie A.-G. in the art of MeOH synthesis. The equipment is described, and operating data are presented in some detail. In general, the process is similar to that used in the United States. Analysis of the feed gas at the entrance to the converter is as follows: CO, 18.4; H_2, 67.2; CO_2, 0.7; CH_4, 0.6; and inerts 13.1%. The maximum operating temperature in the catalyst bed is 360°–390°; the usual operating pressure, 250–260 atm. Approximately 3,000 m.³ of fresh feed are required per ton of crude MeOH produced; the circulation rate approximately 100,000 m.³ per hr. With the new type of converter described the conversion per pass is 12–16% of the CO fed, the yield of MeOH on the basis of the CO fed being approximately 72% and on the H_2, 62%. The catalyst for MeOH synthesis has the following composition: 26–30 Cr_2O_3, 59–64 ZnO, 1–1.5 graphite, and 9–10% H_2O. The method of preparation and reduction is described. Its normal life is 6–12 months. The following utilities are required per ton of crude MeOH: Electricity 25 kw.-hr., steam 0.3 ton, cooling water 130 m.³, and labor 1.54 man-hours.

2832. Roberts, E. C. Precementitic Carbides in Tempered Martensite. Jour. Metals, vol. 188, 1950, Trans., p. 1210.

The 3d stage of tempering quenched steel is the development of cementite from an intermediate, which makes its appearance in the 1st stage. This is not a transition precipitate but a distinct entity with no coherence existing between the carbide and the matrix. It forms faster in quenched martensite than does cementite, and its growth to larger particle size than early Fe_3C must mean that the latter grows as a result of a competitive process.

2833. Roberts, G. Production of Liquid Hydrocarbons and Chemicals From Natural Gas. Oil Gas Jour., vol. 46, No. 26, 1947, p. 40; Petrol. Processing, vol. 2, 1947, pp. 905–906.

Abstract of paper presented at the meeting of the Independent Natural Gas Association of America. Synthetic gasoline from natural gas now is competitive economically with gasoline from crude oil, and if crude oil were to rise approximately $1.00 per bbl., gasoline from coal would then be competitive with petroleum gasoline. Gasoline from coal may become a reality by 1950. Commercial use of the synthesis process will give great impetus to the organic chemical industry. In this connection, the work now being planned for the plant of the Stanolind Oil & Gas Co. at Hugoton is described. Application of the fluid technique to operation of the synthesis process is discussed.

2834. Roberts, G., and Phinney, J. A. Manufacture of Synthetic Gasoline Nearing Commercial Application in United States. Oil Gas Jour., vol. 45, No. 45, 1947, pp. 72–73, 139–141; Petrol. Processing, vol. 2, 1947, p. 312; World Petrol., vol. 18, No. 7, 1947, pp. 46–49; Chem. Abs., vol. 41, 1947, p. 4286.

Paper presented at the American Society of Mechanical Engineers meeting, Tulsa, Okla. An outline is given of the engineering aspects of the commercial synthetic gasoline plants in Germany and of the proposed plants in the United States. It is shown by actual construction data how superior the American engineering techniques are to those of Germany. The investment cost for commercial synthesis plants in Germany was about $7,500–$8,000 per daily bbl. of product, as compared with $3,000–$3,500 in America. In a commercial plant of American design, 6 reactors, each of approximately 3,400 cu. ft. vol., would be required to produce 6,000 bbl. per day of synthetic oil, whereas, by the German technique, about 300 reactor units, each of approximately 950 cu. ft. vol., would be required.

2835. ———. Power-Plant Services for Synthetic Gasoline Manufacture. Power Plant Eng., vol. 51, No. 8, 1947, pp. 108–111; Chem Abs., vol. 41, 1947, p. 7073.

German and American methods for the production of synthetic gasoline are outlined. 2 American methods, 1 using CH_4 with steam and CO_2, and the other CH_4 and O_2 under pressure, are considered. Certain engineering problems are cited. Describes projected plant.

2836. Roberts, G., and Schultz, P. R. Production of Liquid Fuels From Coal and Oil Shale. Oil Gas Jour., vol. 48, No. 19, 1949, pp. 116–125; Petroleum Technol., vol. I, No. 9, 1949, Sec. 1. pp. 24–30.

An economic analysis of comparative costs of liquid fuels from natural gas, oil shale, and coal based on present-day production methods. As a basis for comparison, 5 different raw materials are investigated: Wyoming crude oil, natural gas, oil shale, Indiana bituminous coal, and Montana subbituminous coal. Total direct costs of liquid fuels expressed as cents per gal. of equivalent gasoline are calculated. To the direct costs are added depreciation and tax charges. a major part of the costs of an oil operation. The factual analysis shows that manufacturing costs in bituminous coal, with reference only to Fischer-Tropsch operation, and shale operations would be approximately 80% higher than that made from crude oil, whereas that from subbituminous coal would cost about 125% more. Coal hydrogenation is ruled out. Comparisons of direct cost plus 14% per yr. on the investment show $0.122 for Wyoming crude, $0.15 for natural gas, $0.225 for oil shale, $0.225 for Indiana bituminous coal, and $0.276 for Montana subbituminous coal. It is believed that application of several process improvements now under investigation in the synthesis from coal might lower the cost to a level only $0.05–$0.06 per gal. above present costs of gasoline from petroleum, and that further research might make synthesis nearly competitive.

2837. ———. Liquid Fuels From Coal and Oil Shale. Petrol. Refiner, vol. 29, No. 1, 1950, pp. 104–108.

As a result of an economic study, it is shown that, at present, liquid fuels from oil shale and coal cannot compete with those derived from crude petroleum. Natural gas as a raw material may or may not be competitive, depending on the relative locations of raw-material supply and product markets.

2838. Roberts, J. K. Adsorption of Hydrogen on Tungsten. Proc. Roy. Soc. (London), vol. 152, A, 1935, pp. 445–463; Chem. Abs., vol. 30, 1936, p. 1630.

Method is described for studying the adsorption of H_2 on a bare W surface, which depends on the fact that the accommodation coefficient for Ne is considerably greater for a surface covered with a film of adsorbed gas than for pure W. It is shown that on a clean W surface chemisorption of H_2 occurs very rapidly at temperatures as low as 79° K., saturation of the surface taking place at a partial pressure of 10^{-4} mm. or less. The heat of adsorption as measured on a single fine wire varies from 45,000 cal./mol. for the 1st H_2 mol. to 18,000 for the last portion becoming adsorbed. The amount of H_2 required to form a unimolecular layer is consistent with the adsorption of H as atoms. The film is stable for heating times of about 1 min. up to about 700° K. Calculations show the dipole moment/adsorbed atom to be 1.94×10^{-18} e. s. u. and the change in work function resulting from covering the surface with a complete film to be 5.2 v. The rapidly occurring chemisorption of H_2 on the W surface differs from the more slowly occurring activated adsorption. The accommodation coefficient of Ne at 79° K. is 0.32 on a W surface covered with a layer of chemisorbed H_2 compared to about 0.1 for bare W; at 295° K. the coefficients are, respectively, 0.17 and about 0.08.

2838a. ———. Kinetics of Adsorption With Interaction Between the Adsorbed Particles. Proc. Roy. Soc. (London), vol. A161, 1937, pp. 141–153; Chem. Abs., vol. 31, 1937, pp. 7,719–7,720.

Rate equations, which take into account interaction between adjacent adsorbed particles, are deduced for evaporation and condensation in adsorption both with and without molecular dissociation, and for the formation of a stable, immobile film following dissociation. The nature of the films formed is analyzed, and illustrated by the adsorption of H_2 on W.

———. *See* abs. 3720.

Robertson, A. *See* abs. 1408.

Robey, R. F. *See* abs. 2325a.

2839. Robinet, P. [Hydropolymerization of Carbon Monoxide.] Chim. et ind., vol. 47, 1942, pp. 480–482; Chem. Zentralb., 1942, II, p. 1652; Chem. Abs., vol. 37, 1943, p. 6107.

Following reaction types occur in hydropolymerization of CO:
(1) $2CO+2H_2 \rightarrow CH_2(OH)CHOH_2\ CH_2(OH)\ CH_2OH$;
(2) $2CO+4H_2 \rightarrow C_2H_4+2H_2O$; (3) $4CO+2H_2 \rightarrow C_2H_4+2CO_2$. The synthesis of higher hydrocarbons from water gas at normal pressures is regarded as a combination of (2) and (3). At higher pressures (1) takes place predominantly, with the formation of O-containing compounds. In the reaction mechanism proposed, H_2O is split off before condensation occurs. A primary complex is formed upon the catalyst. At normal pressure this complex decomposes into CH_4. Under the influence of condensing catalysts, an increase in the complex occurs on certain active centers, and the reaction becomes strongly exothermic. If the growth of the complex is not stopped by the cleavage of H_2O or CO_2, the evolution of heat become so great that sudden decomposition of the complex takes place, so that all of the active centers can form only CH_4, H_2O, and CO_2. It is possible that the complex grows not only under the influence of CO and H_2, but under the influence of free radicals that originate simultaneously in other active centers. Thus, not a polymerization of radicals, as contemplated by Fischer, but a kind of copolymerization takes place upon the active centers.

Robitschek, F. O. *See* abs. 587.

2840. Robson, G. W. Benzol Recovery by Active Carbon. Gas Jour., vol. 246, 1945, pp. 687, 689.

Active C plant at the Morpeth Gas Works is described. Its capacity is 400,000 cu. ft. of gas per day, using about 3 cwt. of C in the absorber. A complete cycle of operation has 3 periods: adsorbing, steaming, drying in the time ratio of 60:33:30. The efficiency of extraction is about 90%; this could be raised with careful chemical supervision. The over-all running costs are about 6 d. per gal. of benzol recovered.

Rock. S. M. *See* abs. 1195.

Rockenback, L. P. *See* abs. 3306.

2841. Rode, E. Y. [Iron Oxides and Their Reducibility With Hydrogen and Carbon.] Jour. Russian Phys.-Chem. Soc., vol. 62, 1930, pp. 1453–1466; Chem. Abs., vol. 25, 1931, p. 2628.

Heating curve of Fe_2O_3 has a conversion point at 745°, quite likely corresponding to a definite modification of Fe_2O_3. Beginning with 1,280° some irregularities are observed that probably have a connection with the beginning of loss of O_2. The temperature curve of reduction of Fe_2O_3 with H_2 has 2 kinks, probably corresponding to 2 steps in reduction, 1st to Fe_3O_4 and then to a lower oxide. There is no definite proof of formation of FeO as an intermediate product. Fe_2O_3 is more easily reduced with H_2 than Fe_3O_4. In reducing hydrated Fe oxides with H_2 the point where reduction begins could not be ascertained, because it lies in the region of decomposition of corresponding hydrates. If the products of reduction are cooled in H_2, they become pyrophoric when the heating temperature does not exceed 600°–650°. A higher heating temperature makes them nonpyrophoric. Reduction of Fe_2O_3 and hematite ore with C gives on the temperature curve 3 halts, probably corresponding to 3 consecutive stages of reduction to the metal. Here again Fe_2O_3 is more easily reduced than Fe_3O_4.

2842. Rodillon, G. [Formula Permitting the Unique Calculation of the Boiling Point of Normal Saturated Hydrocarbons C_nH_{2n+2} as a Function of the Number of Carbon Atoms in the Molecule.] Bull. soc. chim., 1950, pp. 839–840; Chem. Abs., vol. 45, 1951, p. 1824.

Following empirical formula was utilized: Log $T_n=(0.5145-0.00122n)\log N+P+1.303$, where T is the boiling point in °K. at 760 mm., n is the number of C atoms, and P is the weight % of C in the molecule. Tabular data were presented, which indicated that the results were accurate to 1°–3° for molecules containing 1–19 C atoms.

2843. Roelen, O. [Temperature Control in Exothermic Gas Reactions.] Brennstoff-Chem., vol. 11, 1930, pp. 68–70; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 577–583; Chem. Abs., vol. 25, 1931, p. 190.

Discussion containing some remarks on the effect of exothermic heat changes on the Fischer-Tropsch synthesis.

2844. ———. [Determination, Conversion, and Removal of Organically Combined Sulfur From Gas.] Brennstoff-Chem., vol. 12, 1931, pp. 305–312; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 466–480; Chem. Abs., vol 25, 1931, p. 5970.

Combustion methods of determination already proposed and modified give low results. Conversion into H_2S by means of various catalysts and types of apparatus becomes incomplete after a short time. CO and H_2S in contact with Fe at various temperatures form volatile S compounds not removable as H_2S from the gas. The catalyst so sulfurized then forms organic S compounds with purified gas even at temperatures as low as 300°. Maximum formation of organic S compounds on passing water gas or coke-oven gas, cracked with steam at high temperatures, over Fe wool occurred at 100°. None formed with CO-free gas or Al or Ag catalyst. The formation of Fe_xS as an intermediate in the formation of COS and CS_2 from H_2S and CO is suggested. For the production of gas low in organic S, coke-oven gas is passed through heated Fe-catalyst contact purifiers, after first passing through CH_4 cracking units where steam at high temperatures also decomposes part of the organic S compounds. Extensive bibliography.

2845. ———. [Manufacture of Magnesium-Containing Catalysts for the Gasoline Synthesis.] FIAT Reel K–25, Nov. 19, 1937, frames 3,827–3,828; PB 70,216: TOM Reel 292.

Direction for wholesale manufacture of Mg-containing catalysts, including a method for the manufacture of Co–Mg–Th–kieselguhr catalysts.

2846. ———. [Alkali Resistance of Kieselguhrs.] FIAT Reel K–29, 1938, frames 7,087–7,090; PB 70,218: TOM Reel 296.

It is established by tests that no causal connection exists between the alkali resistance and the catalytic usefulness of kieselguhrs. 1 table and 3 diagrams.

2847. ———. [Determination of Grit in Kieselguhr.] FIAT Reel K–29, 1938, frames 7,082–7,086; PB 70,218; TOM Reel, 296.

Schulze-Harkert washing method is the only one recommended for the determination of the heavy components. Directions are given for the analytical analysis of a specific type called kieselguhr 120.

2848. ———. [Determination of the Content of Free Metal in Cataylsts.] FIAT Reel K–20, frames 32–37, 1938; PB 70,211; TOM Reel 287.

Co catalysts are not reduced completely; unreduced oxide and carbonate remain. The determination of the proportion of reduced metal is based on the fact that only the reduced metal, when mixed with H_2SO_4, develops an equivalent amount of H_2, which is measured. By determination of the total amount of Co used, the proportion of reduced metal can be calculated. Care must be taken that the N_2 used for the catalyst is free from O_2 and that the H_2 adsorbed on the catalyst is sucked off beforehand in the vacuum. Details, with sketch of apparatus.

2849. ———. [Longevity of Catalysts.] FIAT Reel K–29, 1938, frames 7,030–7,031; PB 70,218; TOM Reel 296.

Successful test on the reactivation of a catalyst for the gasoline synthesis without pressure proves, in principle, the possibility of an extraordinary long catalyst life.

2850. ———. [Preparation of Catalysts.] FIAT Reel K–29, 1938, frames 7,189–7,193; PB 70,218; TOM Reel 296.

Review of the actual state of tests on the improvement in catalyst preparation in the form of an operating instruction for the preparation, especially of Th-free Co–Mg catalysts. 1 picture.

2851. ———. [Report on the Most Favorable Ratio in Cobalt–Kieselguhr Catalysts.] FIAT Reel K–25, May 2, 1938, frames 3,757–3,781; PB 70,216; TOM Reel 292.

Tests and table show that the ratio of 1 : 2 is the best in such catalysts. There is no obvious reason for changing this ratio. Consideration also is given to catalysts of Th–Co–kieselguhr and Th–Mg. Numerous tables and graphs.

2852. ———. [Catalysts for Fischer-Tropsch Synthesis.] FIAT Reel K–20, frames 340–348, Aug. 18, 1939; PB 70, 211; TOM Reel 287.

Development of the gasoline synthesis by the Fischer-Tropsch method is reviewed, and special stress is placed upon the production of a suitable catalyst as being the most important point in the economy of the process.

2853. ———. [Determination of Iron in Catalysts.] FIAT Reel K–29, 1939, frames 6,930–6,931; PB 70,218; TOM Reel 296.

For the determination of Fe in catalysts a 10% acetic acid is recommended as solvent. The determination is based on active Fe and not on the total Fe content.

2854. ———. [Development of Catalysts for the Fischer-Tropsch Synthesis.] FIAT Reel K–29, 1939, frames 6,959–6,967; PB 70,218; TOM Reel 296.

Survey of the history of the development of catalysts for the Fischer-Tropsch synthesis. The survey considers only the usual Fe and Co catalysts and does not give any new catalysts or methods.

2855. ———. [Iron Catalysts in the Gasoline Synthesis.] FIAT Reel K–29, 1939, frames 6,912–6,925; PB 70,218; TOM Reel 296.

Operating experiences with Fe catalysts under pressure in a single passage and in the circulating process are reviewed. 13 diagrams.

2856. ———. [New Method of Cooling Catalyst Furnaces for the Synthesis of Hydrocarbons.] FIAT Reel K–29, 1939, frames 6,936–6,940; PB 70,218; TOM Reel 296.

Reaction temperatures of certain catalysts, for example, Fe catalysts, are very high. The use of H_2O as coolant causes high pressure, therefore the cooling system must have corresponding dimensions. An appropriate fraction of the hydrocarbons prepared by the synthesis process is recommended as cooling medium. Later it is returned to the process.

2857. ———. [Paraffin Synthesis With a New Cobalt Catalyst.] FIAT Reel K–29, 1939, frames 6,941–6,944; PB 70,218; TOM Reel 296.

Description of a new Co catalyst, which gives a very high yield of paraffin, is given. The new catalyst has a very high density of Co and contains Mn as an activator.

2858. ———. [Sulfur Content in Solutions for the Preparation of Cobalt Catalysts.] FIAT Reel K–29, 1939, frames 6,987–6,988; PB 70,218; TOM Reel 296.

It is proved that a % of sulfate up to 8% in pure Co solutions in the preparation of Co catalysts does not reduce perceptibly the activity of the catalyst. In the technical operation, however, one has to take into account a certain Ca content in the Co solutions, which causes, in connection with the H_2SO_4, a plastering and consequently a deterioration of the contact. For this case, an activating washing with dilute alkali solution is recommended.

2859. ———. [Hydrocarbon Synthesis With Iron Catalysts.] TOM Reel 178, Sept. 13, 1940, frames 2,643–2,669; PB 97,330t; Bureau of Mines Transl. T–469, Dec. 29, 1948, 21 pp.; TOM Reel 279, frames 0,127–0,147.

Brief account of the development of Fe catalysts, their operation, as compared with Co catalysts, and some results obtained in pilot-plant operation. Results are tabulated.

2860. ———. [Ruhrchemie Oxo Synthesis.] FIAT Reel K–21, 1940, frames 610–673; PB 70,212; TOM Reel 288.

Reports included review of the possibilities of making higher fatty acids and alcohols from olefinic primary hydrocarbons by means of the Oxo synthesis. Different alcohols are examined as to their chemical-physical qualities. Description and flowsheet are given for the manufacture of fatty alcohols.

2861. ———. [Concentrated Cobalt Catalysts.] FIAT Reel K–29, 1941, frames 7,296–7,301; PB 70,218; TOM Reel 296.

Composition of a catalyst with a high Co density for an increased production of paraffin with the most important data and an exact manufacturing direction.

2862. ———. [Oxo Synthesis Especially for Manufacturing Propyl Aldehyde.] FIAT Reel K–21, frames 1,140–1,146, Nov. 27, 1941; PB 70,212; TOM Reel 288.

A program is set up for the Oxo synthesis. The intention is to make determinations on the advantage of transforming the Co either into its colloidal or very finely distributed form or into carbonyl by previous operating processes.

2863. ———. [Catalysts for the Hydrogenation of Carbon Monoxide.] FIAT Reel K–29, 1943, frames 7,226–7,239; PB 70,218; TOM Reel 296.

Catalytic hydrogenation of CO is reviewed. It is established, above all, that the weakening of the catalyst under normal synthesis conditions during the first 6 months cannot be explained by coarsening changes in the structure.

2864. ———. [Calculation of the Yield in the Synthesis of Higher Hydrocarbons.] FIAT Reel K–29, 1944, frames 7,201–7,209; PB 70,218; TOM Reel 296.

Development of a simplified clear method for the calculation of the yield in synthesis of higher hydrocarbons. Includes formulas.

2865. ———. [Calculations of Gas Utilization and the Course of Synthesis During the Hydrogenation of Carbon Monoxide.] TOM Reel 49, July 1944, frames 470–523; Bureau of Mines Transl. T–420, November 1947, 65 pp.; TOM Reel 274, frames 1,205–1,270.

Gives the basis of a mathematical treatment of the computations of gas utilization during the hydrogenation of CO. The basic relationships between the amounts of raw materials and of the resulting products are explained. These fundamental relationships lead readily to convenient formulae that can be applied algebraically to any additional computations.

2866. ———. [Calculations of Yields in the Modern State of the Synthesis of Higher Hydrocarbons.] TOM Reel 49, August 1944, frames 524–532; Bureau of Mines Transl. T–421, November 1947, 12 pp.; TOM Reel 274, frames 1,271–1,282.

Continuation of the computations discussed in abs. 2865.

2867. ———. [Iron Catalysts.] FIAT Reel K–29, 1944, frames 7,210–7,213; PB 70,218; TOM Reel 296.

Problems of the change from Co to Fe catalyst are discussed. A final result is not formulated.

2868. ———. [Calculation of Gas Consumption and Synthesis Course in the Hydrogenation of Carbon Monoxide.] TOM Reel 134, Navy 5811, Item Ib–3; Bureau of Mines Transl., February 1947, pp. 32–69.

Characteristic properties of a mixture of synthesis gas and reaction products, which describe the course of the synthesis, are discussed, and an appropriate nomenclature is suggested. On the basis of simple stoichiometry, a variety of relationships among these properties is derived. A numerical method for calculation of the yield and related properties from gas analysis data is devised. Methods for testing the accuracy of calculations of the experimental data are developed.

2869. ———. [Calculation of Yield for Higher Hydrocarbons Based on Recent Methods.] TOM Reel 134, Navy 5811, Item Ib–4; Bureau of Mines Transl., February 1947, pp. 70–78.

Methods for calculating the yield and related properties, discussed in item Ib–3, are developed further and compared with the methods employed in Government research.

2870. ———. [Synthesis of Aldehydes and Derivatives From Olefins, Carbon Monoxide, and Hydrogen.] Angew. Chem., vol. 60, 1948, A, p. 62; British Abs., 1949, A, II, p. 3.

Reaction of olefins with CO and H_2 over Co or Fe, to give aldehydes containing 1 C atom more than the olefin, is described in detail. C_2H_4 with CO and H_2 in equivalent proportions, with a Co catalyst, at 115° and not less than 100 atm., gives 75% EtCHO. Byproducts include aldol condensation products and below 100°, $COEt_2$. Above 200°, C_2H_6 and PrOH are obtained over a Co–Cu catalyst. Only Fe may replace Co as catalyst. It should be introduced or generated in finely divided form. The actual catalysts are metal carbonyls, which may replace the metal, thus enabling lower reaction pressures to be used. Water gas may replace CO and H_2. Production of aldehydes is a general reaction of olefins. Higher olefins react best at 130°–150° and give less byproducts than does C_2H_4. Unsymmetrical olefins may give a mixture of 2 isomeric aldehydes, but steric factors may suppress the formation of 1 of them. Aldehydes, C_4–C_{24}, can be obtained from the olefins produced in the Fischer-Tropsch synthesis and can be reduced readily, without isolation, over similar Co catalysts to the corresponding alcohols. Derivatives of these products and their possible industrial applications are listed. C_2H_2 and water gas over Co at 140°–150° and 10 atm. give 120 gm. per m.^{3} liquid products. Chiefly they are unsaturated secondary products of higher molecular weight. No experimental details.

2871. ———. [Cobalt and Nickel Catalysts for the Hydrogenation of Carbon Monoxide.] Angew. Chem., vol. 61, 1949, p. 448.

Paper presented at the annual meeting of the German Chemical Society in September 1949. The best method for producing highly active catalysts from Co is by precipitation of the carbonate from boiling nitrate solution upon kieselguhr. Newly roasted kieselguhr from finely divided crude kieselguhr with a minimum amount of impurities makes the best carrier. The particle size of the carrier influences the boiling properties of the products and the paraffin deposition on the catalyst. The 3 best activators for Co are Th, Mg, and Mn. Th and Mn promote the formation of high-molecular hydrocarbons and the deposition of paraffin on the catalyst, whereas Mg has the opposite effect. Further specific effects were determined. The technically best catalyst contains both Th and Mg. The highest activity, measured by the temperature, is shown by Mn with complete conversion already at 160°. Co oxide can, under the best conditions, be reduced below 250°; at 400° complete reduction occurs in 1 min. The mechanism of the poisoning of the catalyst by impurities was explained; it occurs only in the afterheating period of reduction, neither before nor after. The Co solution must contain no Cu, Fe, Al, and Ca. These metals are removed by wet regeneration. The temporary disabling of the catalyst because of paraffin deposition can be removed through destructive hydrogenation or extraction. C deposition was acknowledged as the reason for any remaining poisoning rather than recrystallization or the like. Dry regeneration by removing the deposited C by means of H_2 at 400° gave complete reactivation. Repeated dry regeneration produced operating periods of over 2 yr. without exhaustion of the catalyst. Highly active Co catalysts decompose CO at temperatures as low as 30°. Mg is able to activate Ni catalysts also. The first technical methanation was realized with a Ni–Mg–kieselguhr catalyst.

2872. ———. [Determination of Double Bonds and Their Terminal Constituents in Hydrocarbons by Ozonization and the Application of This Method to the Determination of the Olefin Distribution in Fischer-Tropsch Products.] Erdöl u. Kohle, vol. 3, 1950, p. 591.

Abstract of a paper presented at the 3d meeting of Die deutsche Gesellschaft für Mineralölwissenschaft und Kohlechemie. Olefinic double bonds can be determined by weight analysis by adding ozone and ascertaining the increase in weight. The method gives accurate and reliable values, in many cases even when the addition of halogens fails to work. Terminal double bonds were determined by cracking the ozonides obtained as previously and determining the formic acid produced. With Fischer-Tropsch products, the characteristic dependence of the α–olefin constituents upon the production conditions and the size of the molecules was established in this manner. The experimental results also support the theory for the range of molecules above C_6, whereby primary α–olefins are formed in the hydrogenation of CO and are finally partly isomerized.

2873. ———. [Synthesis of Methane in Connection With the Production and Utilization of City Gas.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 10.

Paper presented at the 1949 meeting of Diedeutsche Gesellschaft für Mineraloelwissenschaft und Kohlechemie. The necessity of producing more city gas without increasing the amount of coke has led to attempts to bring the Fischer-Tropsch synthesis into city gas production. The synthesis can be so conducted that it produces directly a residual gas of city-gas quality, or the necessary heating value of the synthesis residual gas can be obtained by a special methanization. New Fe and Ni catalysts have been developed for the various possible ways of operating. CH_4 synthesis can now be conducted by choice from CO and H_2 with exclusive formation of H_2O or CO_2, from CO and steam with simultaneous conversion, or by any combination whatever of these 3 reactions. A new Ni–Mg catalyst methanizes the CO and CO_2 in coke oven gas quantitatively below 200° and at gas throughputs 10 times greater than the former technical Fischer-Tropsch synthesis. By means of a NiS catalyst it is now possible to desulfurize coke-oven gas to a synthesis gas purity. With these 2 new Ni catalysts methanization of city gas could be successfully realized at the storage tank in small automatic plants. By such means, the heating value is raised from about 4,400 to 6.000 kg.-cal. per m.^{3} The gas is detoxicated at the same time and freed from all corroding constituents except hydrocyanic acid. The original tank plants for methanizing in Altenessen, 1942, have already been followed by others.

———. *See* abs. 341, 402, 1042, 1214, 1334, 1335, 3729.

2874. ROELEN, O., AND FEISST, W. [Improved Method for the Determination of Sulfur in Gas.] Brennstoff-Chem., vol. 15, 1934, pp. 187–192; Chem. Abs., vol. 28, 1934, p. 6278.

Method of Heinrich and Petzold for the determination of total or organic combined S has been improved mechanically, to permit greatly increased throughput and absorption in alkaline H_2O_2. Apparatus for the