process can be so regulated that the molecular complexity of the paraffins formed is to some extent controlled; that is, one can produce mainly casinghead gas or benzine with higher homologs as desired. Boiling ranges of the products are given. The authors believe the catalytic process involves formation of a carbide rich in C as a first stage (Fe_3C_4 or Fe_2C_3), which is afterward reduced to CH_2. This polymerizes in the presence of H_2 to form saturated paraffins. From the reaction $3CO+3H_2=CO_2+H_2O+2CH_2$, 190 gm. of hydrocarbons are obtainable from 1 $m.^3$ of water gas. 100 gm. of liquid hydrocarbons of benzine character were obtained by passing 1 $m.^3$ of water gas several times over an Fe–Co contact mass. The process may be used primarily for the manufacture of petroleum products, especially motor spirit, or as an adjunct to water-gas plants for gas enrichment.

1022. ———. [Aluminum Oven for Contact Reactions.] Ztschr. angew. Chem., vol. 40, 1927, p. 1204; Brennstoff-Chem., vol. 8, 1927, pp. 323–324; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 308–310; Chem. Abs., vol. 22, 1928, pp. 701, 1253.

The block oven is an Al rod 500 mm. long and 80 mm. diameter with a central longitudinal hole 24 mm. diameter and is insulated with diatomaceous earth and heated with gas burners with automatic temperature control. The segment oven differs in having the tube cut into 10 segments separated by asbestos plates so that each segment may be held at a different constant temperature. An Ostwald thermoregulator keeps the temperature constant. Because of high heat capacity and condition of Al, the temperature can be held uniform (within 1° at 240°) throughout the length of the bore.

1023. ———. [Formation of Synthol on Carrying Out the Petroleum Synthesis Under Pressure and the Synthesis of Hydrocarbons of High Molecular Weight From Water Gas.] Brennstoff-Chem., vol. 8, 1927, pp. 165–167; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 209–214; Chem. Abs., vol. 22, 1928, p. 497.

Results are reported from which it seems clear that products obtained catalytically at pressures of 10–15 atm. are intermediate in character. They were neither exclusively hydrocarbons, as in the atmospheric pressure synthesis, nor mainly oxygenated compounds, as the high-pressure synthol synthesis. A disadvantage of working at 10–15 atm. is that paraffins of high molecular weight are retained by the catalyst, rendering it inactive in time. A paraffin, $C_{70}H_{144}$ was isolated.

1024. ———. [Composition of Products Obtained by the Petroleum Synthesis.] Brennstoff-Chem., vol. 9, 1928, pp. 21–24; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 523–533; British Chem. Abs., 1928, B, p. 324; Chem. Abs., vol. 22, 1928, p. 2657.

Composition of gases (gasols) varied with the catalyst and conditions of the experiment. A gas obtained with a Fe–Cu catalyst showed the following composition by condensation analysis: C_3H_8, 42.5; C_2H_6, 19.5; C_4H_{10}, 2.0; C_2H_4, 6.0; C_3H_6, 21.0; and C_4H_8, 9.0%. Benzine, boiling 60°–185°, recovered by adsorption in active charcoal and steaming out at 250°, contained 30% paraffins, for the most part octane, nonane, and isononane, which were positively identified. The remaining 70% of the benzine were olefins. There were no diolefins present. Heavier products were examined only for unsaturation by the Wijs I method. The degree of saturation could be varied by varying the catalysts or experimental conditions; for example, doubling the gas space velocity increased the unsaturation of the oil 3 times. Water-soluble oxygenated products (aldehyde and acetone) amounted to 2% of total products recovered. There was no trace of compounds of ring structure found. All products could be converted into paraffins by hydrogenation in contact with Ni. The mechanism of the catalytic petroleum synthesis is discussed. In addition to the two previous assumptions of reaction mechanism, the carbide—CH_2, and the molecular complex theories, a third possibility is advanced—the primary formation of high-molecular hydrocarbons and their subsequent catalytic cracking into lower hydrocarbons. In all 3 cases, unsaturated hydrocarbons temporarily occur and then are subjected to a greater or less extent to hydrogenation.

1025. ———. [Conversion of Methane Into Hydrogen and Carbon Monoxide.] Brennstoff-Chem., vol. 9, 1928, pp. 39–46; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 583–602; British Chem. Abs., 1928, B, p. 322; Chem. Abs., vol. 22, 1928, p. 2652.

Mixtures of CH_4 with CO_2 and CH_4 with coke-oven gas and coke-oven gas with water vapor were decomposed by various catalysts (Fe, Co, Ni, Cu, Mo, and W) supported on clay, silica, and $MgCO_3$ or mixed with Al_2O_3. Temperatures 840°–920° were used with various space velocities, throughput in cc. per hr. divided by catalyst volume in cc.; the best space velocity for decomposition of oven gas-steam mixtures was 800. In no case was CH_4 completely decomposed. An example of good conversion of an oven gas-CO_2 mixture at 860° is given by the following analyses of original gas and the products, respectively: CO_2, 18.0, 1.4%; heavy hydrocarbons, 1.0, 0.0; O_2, 1.7, 0.2; CO, 5.1, 33.2; H_2, 41.7, 56.6; CH_4, 19.6, 1.4; N_2, 12.9, 7.2. The catalyst was Ni supported on silica. Fe, Cu, Mo, and W were poor catalysts. Co proved as good as Ni, contrary to literature. Activity of Ni and Co was increased by addition of Al_2O_3. Clay proved best as a carrier for active metals.

1026. ———. [Petroleum Syntheses.] Ges Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 313–501; Chem. Zentralb., 1932, II, p. 2569; Chem. Abs., vol. 27; 1933, p. 5950.

Collection of the experiments of the authors on petroleum synthesis up to 1928 (see abs. 1021). Gas purification, the question of catalyzers and the operating conditions (temperature, pressure, poisoning of catalyzers) influencing the reaction are treated exhaustively.

1027. Fischer, F., and Wangenheim, F. [Reactions Between Carbon Monoxide, Carbon Dioxide and Hydrogen in a "Cold-Warm" Tube at Atmospheric and High Pressures.] Brennstoff-Chem., vol. 9, 1928, pp. 94–97; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 570–579; British Chem. Abs., 1928, B, p. 355; Chem. Abs., vol. 22, 1928, p. 4323.

Special steel bomb is used in which the contact metals serve as electric resistors. Metals used were: Fe, Ni, W, Mo, and also C, named in order of their catalytic activity. Various mixtures of CO and CO_2 with H_2 were used. C was produced and also CH_4, with traces of higher homologs in some cases. Traces of HCHO were formed but no CH_3OH. Temperatures of 550°–800° were used.

1028. ———. [Some Gas Reactions in a "Cold-Warm" Tube.] Brennstoff-Chem., vol. 9, 1928, pp. 97–98; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 580–582; Chem. Abs., vol. 22, 1928, p. 4323.

Apparatus designed (abs. 1027) to investigate catalytic reactions of mixtures of CO and H_2 was used with Fe as a catalyst. Mixtures of CO, CO_2, H_2O, and CH_4 were investigated at 600°–700° and up to 6 atm. CH_4 remained practically unchanged. Reactions taking place were: (1) $2CO \rightarrow CO_2+C$ and (2) $CO+H_2O \rightarrow CO+H_2$.

1029. Fischer, F., and Weinrotter, F. [Thermal Cracking of Kogasin to Gaseous Olefinic Hydrocarbons.] Brennstoff-Chem., vol. 21, 1940, pp. 209[217; Chem. Abs., vol. 35, 1941, p. 8253.

Previous work is reviewed briefly. The work of Fischer with Peters and Winzer is continued, and it is shown that at low-glow temperatures, with Pt wire spirals electrically heated, over 50% by weight of Kogasin II can be cracked into higher olefins. Including C_2H_4, the content of the cracked gases is around 90% of unsaturated hydrocarbons. Lowering of the glow-element temperatures does not increase the olefinic yield but increases the proportion of saturated hydrocarbons. At higher temperatures about 70% olefinic yield is obtained but with more C_2H_4 at the expense of the higher members. Similar results were obtained with a Pythagoras tube at 675°–760°, but only part of the Kogasin vapor was cracked in the recirculatory system, thereby interfering with further cracking of the initially formed olefins. Cracking in vacuo gave no different results with the wire spiral. A low-temperature fractionating column for analyzing the gas mixtures is described in detail with operating procedure. The Podbielniak dephlegmator for automatically maintaining desired temperatures with liquid air was employed. Analytical curves are presented of the operation. Sharp separations of the C_2, C_3, C_4 hydrocarbons were obtained. Saturated and unsaturated hydrocarbons were separated by absorption of the latter in $Hg(NO_3)_2$ solution, the H_2 and CH_4 being separated previously and subjected to combustion analysis. 13 refs.

1030. Fischer, F., Bahr, T., and Meusel, A. [Catalytic Reduction of Carbon Dioxide to Methane and Higher Hydrocarbons at Ordinary Pressure. Preliminary Communication.] Brennstoff-Chem., vol. 16, 1935, pp. 466–469; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 263–270; Chem. Abs., vol. 30, 1936, p. 3967.

When Ru powder or Ru–Th asbestos is used as contact catalyst, CO_2 may be appreciably reduced to CH_4 from 100° upward. Addition of $CaCO_3$ or Rb_2CO_3 results in the formation, from 170° upward, of higher gaseous and fluid hydrocarbons. Weaker alkalies do not have this effect on the catalyst.

1031. ———. [Catalytic Reduction of Carbon Dioxide to Higher Hydrocarbons at Atmospheric Pressure.] Ber. deut. chem. Gesell., vol. 69 B, 1936, pp. 183–186; Chem. Abs., vol. 30, 1936, p. 3401.

Hitherto it was not possible to reduce CO_2 to higher hydrocarbons than CH_4, but it has now been found that this can be accomplished with a Ru catalyst to which have been added small amounts of alkali. It had already been shown that in the active form in which it has recently been employed, Ru catalyzes the reduction of CO_2 even at 100°, but at these low temperatures, only CH_4 is formed. Quite different is its behavior if alkali, for example, 2% K_2CO_3, is added to it. The temperature of incipient CO_2 reduction is thereby raised to 150°, and beginning at 170°–180° there are formed not only CH_4 but also higher gaseous and liquid hydrocarbons. There are deposited at the end of the reaction tube first a colorless, low-boiling oil, later a higher-boiling oil, and finally paraffin-like products. The oil and water formed are at first neutral or faintly acid; later, increasing amounts of acid products with the odor of the lower fatty acids are produced. The gaseous products formed at 180°–225° contain 1.32–1.45 C atoms. The most favorable temperature range for the production of an oil seems to be 200°–225°, although higher hydrocarbons can still be detected at 300°; above this temperature only CH_4 is formed. The reactivity of the catalyst decreases quite rapidly, and the catalyst must be regenerated by passing air at 300°–400° over it. Comparative experiments on the influence of the amount and nature of the alkali on the catalytic behavior of Ru showed that 0.5% K_2CO_3 was not enough to impart an oil-producing power; Li_2CO_3 up to 3% and Na_2CO_3 up to 1.5% were likewise ineffective. Rb_2CO_3 (3.4%) had the same effect as K_2CO_3. Ru with 2.9% $KAlO_2$ at 200° first gave only CH_4, but after about 20 hr. CH_4 homologs and liquid hydrocarbons began to be formed; at lower temperatures (180°) there were no detectable amounts of oil even after 66 hr. and only small amounts of acid products. The formation of higher hydrocarbons by alkalized Ru is believed to proceed through CO, to which the catalyst first reduces the CO_2. From analogy with the metals of the Fe group, it would seem probable that the catalyst is a carbide, although no Ru carbide is as yet known.

1032. Fischer, F., Koch, H., and Wiedeking, K. [Advances in the Preparation of Lubricating Oils, Starting With Kogasin.] Brennstoff-Chem., vol. 15, 1934, pp. 229–233; Fuel Econ., vol. 10, 1934, pp. 602–604; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 455–465; British Chem. Abs., 1934, B, p. 744; Chem. Abs., vol. 28, 1934, p. 6291.

Relation of viscosity to temperature of lubricants prepared from chlorinated Kogasin condensed with xylene has been improved by increasing the paraffin content. Lubricants possessing properties of paraffin-base oils were obtained in the treatment of Kogasin of Cl content averaging 1–2 atoms with activated Al without the addition of aromatic hydrocarbons. Olefin hydrocarbons in synthetic benzine were polymerized to lubricants by H_2O-free $AlCl_3$, their viscosity depending on the boiling point of the original material. The synthetic lubricants correspond with the best petroleum products in stability toward oxidation, coking residue, and behavior at low temperatures.

1033. ———. Recent Advances in Manufacture of Synthetic Lubricants From Kogasin. Petrol. Refiner, vol. 23, 1944, pp. 312–316; Brennstoff-Chem., vol. 15, 1934, pp. 229–233; U. O. P. Co. Lib. Bull., abs. 34, 1944; Chem. Abs., vol. 38, 1944, p. 5389.

Gasol from the Fischer-Tropsch synthesis, converted into various chloroderivatives, is easily caused to react with aromatic hydrocarbons and an $AlCl_3$ catalyst to produce synthetic lubricants fluid at low temperatures, is very resistant to oxidation, but also susceptible to temperature changes. 3 methods are described for improving the product. The conclusions are that satisfactory high-grade lubricants may be made by gasification of any solid fuel by way of Kogasin synthesis without rejecting any fractions as unsuitable. Products of these improved processes show stability against oxidation, C residue, and pour point and compare favorably with the products of crude petroleum.

1034. Fischer, F., Peters, K., and Koch, H. [Formation of Liquid Hydrocarbons From Acetylene. II. Catalytic Hydrogenation and Condensation of Acetylene.] Brennstoff-Chem., vol. 10, 1929, pp. 383–385; Chem. Abs., vol. 24, 1930, p. 4918.

C_2H_2 (10%) in water gas was passed over Fe–Cu alkali catalyst prepared from the nitrates heated in O_2 at 250°. The yield of 40–70% of the C_2H_2 consisted of benzine and oil, 2:1, the former being recovered from the activated C in which it was collected by distillation to 300° and condensation with liquid air. The oil separated and was collected in a trap. Since the catalyst was not easily poisoned, the water gas was not purified, pure H_2 giving identical yields but lighter colored oils. In a ratio >10:1 of Cu:Fe, cuprene formed and caused clogging. Adding 1 part Ni lessened this, 50–55% of the C_2H_2 producing benzine:oil=3:1, as against 40% for Cu–Fe alone; the contraction was 22% in both cases. Fe alone gave no results below 340°, then produced 35–40% oil with C also separating. With Co, CH_4 was formed quantitatively. Fe:Ni, 2:1, raised the proportion of benzine in the yield to 85–90%, the total yield at 250° being 30–35% of the C_2H_2 used. Contraction in volume, measured by flowmeters, due to the formation of C_2H_6 was 26% (90% of the C_2H_2) but fell to 12% at the end with the formation of C_2H_4 and higher unsaturated compounds. Fe : Ni, 10 : 1, was used 2 months at 250° without regeneration, the contraction, however, falling from 22–23% to 14–15% after that time with still no C_2H_2 passing. The products recovered, benzine : oil as 2 : 1, averaged 60% of the C_2H_2 used. Changes in temperature and velocity had little effect on yield or quality, the higher velocities increasing the proportion of benzine to oil. 90% benzine boiled 50°–150° and consisted of 60% unsaturated compounds. The heavy oil obtained contained no paraffin wax. 1 m.³ of coal gas passed first through an electric discharge and then over heated catalyst gave 85 gm. oil, of which 75% was light oil, losing thereby only 10% of its heating value.

1035. Fischer, F., Peters, K., and Winzer, K. [Thermal Splitting of Higher Paraffin Hydrocarbons Upon a Glowing Wire.] Brennstoff-Chem., vol. 16, 1935, pp. 421–429; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 486–503; Chem. Abs., vol. 30, 1936, p. 3991.

Kogasin II and various fractions were passed as vapor over heated wires of various metals at 1–10 atm. With Pt wire, 20% of light benzene and 80% of gaseous products were obtained; the gas contained over 70% of unsaturated hydrocarbons. C did not separate.

1036. Fischer, F., Pichler, H., and Dienst, W. [Approach to Theoretically Possible Yields in the Fischer-Pichler Intermediate-Pressure Synthesis.] Brennstoff-Chem., vol. 20, 1939, pp. 221–228; British Chem. Abs., 1939, B, p. 904; Chem. Abs., vol. 34, 1940, p. 3904.

Synthesis was effected in two stages at 175°–205° under 10 atm., with a Co–ThO_2–kieselguhr catalyst; products condensable at room temperature were removed after the 1st stage. 2 reaction tubes (internal diam. 10 mm. length of catalyst column 50 cm.) were used in parallel in the 1st stage, and a single similar tube was used in the 2d. The reaction tubes, arranged vertically, were heated by circulating hot H_2O, under pressure, through surrounding jackets. With a throughput of 2 l. of gas, $CO+2H_2$ per gm. of Co per hr., the maximum yield was 140–150 gm. of product, wax 14, liquid hydrocarbons 73, gasol 13% per m.³ of inert-free gas: with a throughput of 0.2 l. per gm. of Co per hr. the maximum yield was 190 gm. of product, wax 48, liquid hydrocarbons 44, gasol 8% per m.³ of gas; the latter yield represents 90% of the theoretical. A decrease in the rate of gas throughput necessitates a lowering of the reaction temperature to obtain the maximum yield of hydrocarbons; at the same time there is an increase in the relative proportion of higher-boiling hydrocarbons in the product. The reaction mechanism is discussed.

Fischer, F., Pichler, H., and Köbel, *H.* [Mixed Gas for Benzine Synthesis. II. Semitechnical Investigation of the Preparation of Mixed Gas for Benzine Synthesis by Simultaneous Conversion of Coke-Oven Gas and Steam Over Coke in the Generator.] *See* abs. 1040.

Fischer, F., Pichler, H., and Köbel, H. [Mixed Gas for Benzine Synthesis. III. Preparation of Mixed Gas for Benzine Synthesis by Simultaneous Conversion of Coke-Oven Gas and Steam Over Coke in the Generator.] *See* abs. 1041.

1037. Fischer, F., Pichler, H., and Lohmar, W. [Synthesis of Kogasin and Paraffin Wax in the Aqueous Phase.] Brennstoff-Chem., vol. 20, 1939, pp. 247–250; British Chem. Abs., 1939, B. p. 904; Chem. Abs., vol. 34, 1940, p. 3904.

By passing $CO+2H_2$ through H_2O containing either a Co–ThO_2 or a Rh catalysts in suspension, at 170°–200° under a total pressure of 50–100 atm., liquid hydrocarbons and wax were obtained similar in yield and composition to the products of the medium-pressure Fischer synthesis (abs. 1036). A laboratory apparatus of 1 l. capacity was used. Ni was useless as a catalyst, being converted into the carbonyl under the reaction conditions; an Fe catalyst merely brought about the reaction $CO+H_2O=CO_2+H_2$. Although by operating in the aqueous phase the temperature control was very good, the process had disadvantages that precluded its practical development; for example, the results were no better than in the dry phase, a relatively larger reaction space was required, the apparatus had to be lined with acid-resistant material (for example, Cu), owing to the production of small quantities of fatty acids, considerable energy expenditure was necessary to maintain the catalyst in suspension, and the continuous removal of the reaction products presented difficulties.

1038. Fischer, F., Pichler, H., and Reder, R. [Influence of Catalytic Admixtures and Reduced Pressures Upon the Setting-Up of the Producer-Gas Equilibrium for Semicoke.] Brennstoff-Chem., vol. 13, 1932, pp. 346–350; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 358–368; Chem. Abs., vol. 26, 1932, p. 5734.

Equilibrium $C+CO_2 \rightleftharpoons 2CO$ was studied with graphite at pressures <20 mm. Hg, 500°–700°; it shifts almost completely to the right at reduced pressure. With semicoke from brown-coal briquets degasified at temperatures 50° higher, the shift was even more complete. Additions of 5% Fe and Al oxides, Ca, Na, and K carbonates to degasified semicoke greatly increased the rate of reaction with CO_2 at atmospheric pressure, this effect increasing with the basicity of the catalyst.

1039. ———. [Mixed Gas for Benzine Synthesis. I. Survey of the Possibilities of Supply of Suitable Carbon Monoxide–Hydrogen Mixtures for the Benzine Synthesis on Grounds of the Present-Day Position of Science and Technique.] Brennstoff-Chem., vol. 13, 1932, pp. 421–428; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 481–496; British Chem. Abs., 1933, B, p. 49; Chem. Abs., vol. 27, 1933, p. 2017.

Use of various technically available gases and mixtures is examined practically and theoretically. Gas mixtures containing CO and H_2 in approximately the ratio of 1 : 2 may be produced by mixing coke-oven gas with generator gas or with water gas (Mischgas), which may be produced simultaneously in the coke oven by the direct gasification of coal or by the interaction of CH_4 with steam and/or CO_2 or O_2, etc. Heat balances have been drawn up for the more important of these processes. The influence of temperature and pressure upon equilibrium and reaction rate has been determined for the cracking of CH_4 by steam over Ni–Al catalyst at 800° per 1 atm. or at 600° per 0.1 atm. with a contact time of less than 1 sec. The effects of temperature and coke activity upon the conversion of coke-oven gas with steam over coke have been determined. A scheme for using coke-oven gas thus regenerated is proposed.

1040. Fischer, F., Pichler, M., and Köbel, H. [Mixed Gas for Benzine Synthesis. II. Semitechnical Investigation of the Preparation of Mixed Gas for Benzine Synthesis by Simultaneous Conversion of Coke-Oven Gas and Steam Over Coke in the Generator.] Brennstoff-Chem., vol. 16, 1935, pp. 331–333; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 322–327; Chem. Abs., vol. 30, 1936, p. 3970.

Apparatus, etc., previously described in abs. 1039 have been improved. Varying the gas : steam ratio gives variation of the CO : H_2 ratio from 1 : 2 to 2 : 7 in the product for benzine synthesis.

1041. ———. [Mixed Gas for Benzine Synthesis. III. Preparation of Mixed Gas for Benzine Synthesis by Simultaneous Conversion of Coke-Oven Gas and Steam Over Coke in the Generator.] Brennstoff-Chem., vol. 16, 1935, pp. 401–404; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 327–333; Chem. Abs., vol. 30, 1936, p. 3970.

In a generator larger than previously used, having a capacity of 100 m.³ per hr., it was possible, through the simultaneous conversion of coke-oven gas and coke with steam, to produce a gas containing CO and H_2 in the correct proportion of 1 : 2 suitable for benzine synthesis. 1 m.³ of coke-oven gas in a mixture with water gas produces 3m.³ of synthesis gas.

1042. Fischer, F., Roelen, O., and Feisst, W. [Present Technical Position of the Benzine Synthesis.] Brennstoff-Chem., vol. 13, 1932, pp. 461–468; Petrol. Refiner, vol. 22, 1943, pp. 429–436; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 501–516; U. O. P. Co. Lib. Bull., No. 1, 1944; British Chem. Abs., 1933, B, p. 136; Chem. Abs., vol. 27, 1933, p. 2017; vol. 38, 1944, p. 1089.

Recent developments in the production of a suitable initial gas mixture, in the method of gas purification and in the preparation of the catalyst are reviewed. The difficulty of temperature control in large-scale apparatus has been overcome by the design of a narrow, rectangular unit contact apparatus, 20 mm. by 120 cm. in cross-section and 5 m. long, which is packed with the catalyst (Ni–Mn–Al_2O_3) and maintained at the reaction temperature, 190°–210°, by the circulation of hot oil around it; the temperature control was made automatic without difficulty, and the apparatus then required little supervision. The yield, 70 gm. of liquid product per m.³ of gas, CO 24%, H_2 48%, was equal to that obtained in the laboratory-scale apparatus. After about 1,000 hr. operation the catalyst required regenerating by extraction of the deposited paraffin wax with light petroleum. By using a battery of such units the throughput of the plant could be increased to any desired value.

1043. Fischer, F., Tropsch, H., and Dilthey, P. [Reducation of Carbon Monoxide to Methane in the Presence of Various Metals.] Brennstoff-Chem., vol. 6, 1925, pp. 265–271; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 175–190; Jour. Chem. Soc., 1925, II, p. 982; Chem. Abs., vol. 19, 1925, p. 3367.

Various metals reduced at low temperature from the oxides where possible, (Co, Fe, Mo, W, Ru, Pd, Os, Ir, Pt, Ag, Cu, Rh), were tested with and without admixture of Al_2O_3 at various temperatures, 100°–800°, for conversion of CO and H_2 mixtures to CH_4. Ru gave the best results, that is, 34.4% CH_4 in exit gas at 300° with a mixture $CO_2 : H_2=1 : 5$ at 12 cc. gas flow per min. The use of Al_2O_3 as a carrier of metals proved advantageous particularly in the case of Fe. The order of the catalytic activity of the metals tested was Ru, Ir, Rh, Ni, Co, Os, Pt, Fe, Mo, Pd, Ag.

1044. Fischer, F., Tropsch, H., and Mohr, W. [Reduction of Carbon Monoxide to Methane in the Presence of Iron at Ordinary Pressure.] Brennstoff-Chem., vol. 4, 1923, p. 197; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 473–474; Chem. Abs., vol. 18, 1924, p. 349.

Reduction of CO to CH_4 by means of Fe as a contact substance takes place in small amount at 400° and 2 atm. This investigation was made to discover whether this reduction would take place at atmospheric pressure and at 400°–550°. The amount of CH_4 formed was in all cases less than 1.0%.

1045. Fischer, F., Tropsch, H., and Schellenberg, A. [Decomposition of Barium, Magnesium, and Lithium Formates.] Ges. Abhandl. Kenntnis Kohle, vol. 6, 1921, pp. 355–359; Chem. Abs., vol. 18, 1924, p. 3170.

Ba formate decomposes in the Al distillation apparatus at 350°–375° with considerable frothing; 45.4 gm. gave 2.2 gm. of MeOH and 0.1 gm. of oil, the residue containing some C. On decomposing Ba formate with superheated steam the aqueous distillate contained HCHO and HCO_2H. Contrary to Berthelot's statement, the gas contained no CH_4 and no unsaturated hydrocarbons. Mg formate decomposed at 400°–425°, giving an aqueous distillate; the residue and gas together contained 1.36 gm.-atoms of C per gm.-mol. of formate. Li formate decomposed at 350°, giving an alcoholic liquid but no oil. Heated with H_2O under pressure at 350°, it gave only gaseous products and carbonate.

1046. ———. [Formation and Decomposition of Calcium Formate.] Ges. Abhandl. Kenntnis Kohle, vol. 6, 1921, pp. 330–354; Chem. Abs., vol. 18, 1924, p. 3170.

Ca formate is obtained in practically theoretical yield on shaking 8 *N* milk of lime with CO under 20–50 atm. at 160° for 12–17 hr. At 180° the Fe parts of the autoclave are seriously attacked. When Ca formate was decomposed at 420°–430° (26 gm. in 1–2 hr.) in the Al distillation apparatus, the residue consisted almost completely of $CaCO_3$, with very small quantities of oxalate and undecomposed formate, and traces of carbonaceous products. The primary formation of oxalate (abs. 3561 and 3564) could not be confirmed. One gm.-mol. of pure Ca formate gave 1.02 gm.-atoms of C in the residue, 0.54 gm.-atom in the gas (which consisted of 47.9% CO, 2.0% CH_4, and 23.8% H_2) 0.20 gm.-atom in the MeOH, and 0.13 gm.-atom in the oil. A mixture of equal parts of Ca formate and CaO gave a rather higher yield of MeOH and less oil, but the addition of more CaO (up to 10 pts.) decreased the yield of MeOH. By carrying out the decomposition of Ca formate in a current of steam, MeOH was obtained in 52% yield. When decomposed in a large Al distillation apparatus 390 gm. of Ca formate gave 15.2 gm. of MeOH containing a small proportion of acetone and 5.5 gm. of oil, of which 2.56 gm. were volatile in steam.

1047. Fischer, F., Tropsch, H., and Ter-Nedden, W. [Synthesis of Paraffin Hydrocarbons of High Molecular Weight From Carbon Monoxide.] Ber. deut. chem. Gesell., vol. 60B, 1927, pp. 1330–1334; Chem. Abs., vol. 21, 1927, p. 2870.

It has already been mentioned that in the preparation of petroleum hydrocarbons from CO solid paraffin hydrocarbons are found in the contact substances (abs. 1020). In 1 of the usual contact substances, which had been treated for a long time with water gas under 10 atm., there were formed, together with the liquid and solid products, which distilled off with the current of water gas, considerable amounts of nonvolatile compounds, and when the experiment was continued a long time, the contact mass increased greatly in weight, and on opening the contact tube, it was found to contain a mass that was solid at room temperature and became semiliquid on warming; on distillation *in vacuo* large amounts of solid paraffin passed over. A part of the product was so difficultly volatile, however, that it was necessary to extract the contact mass with solvents (C_6H_6, xylene). A partial separation was effected into a less soluble fraction melting 104°–117°, solidifying 109°. Its composition, solidification point, and molecular weight all showed conclusively that it consisted of paraffin hydrocarbons of high molecular weight, around 1,000 or about C_{70}.

1048. Fischer, F., Pichler, H., Meyer, K., and Koch, H. [Synthesis of Aromatic Hydrocarbons From Methane at Atmospheric Pressure and Without Catalysts.] Brennstoff-Chem., vol. 9, 1928, pp. 309–316; Proc. 2d Internat. Conf. Bituminous Coal, vol. 2, 1928, pp. 789–807; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 603–625; Chem. Abs., vol. 23, 1929, p. 2694.

Pure CH_4 from various sources and CH_4 with other gases (coal gas) is decomposed by passage through porcelain or quartz tubes heated 900°–1,200°. The tar formed is precipitated by a Cottrell precipitator and light oils are absorbed by active charcoal. The time of contact is fully as important as the temperature. For example, 346 l. CH_4 (89% with 8% N_2) passed through the 1-mm. annular space between concentric 14- and 16-mm. tubes 22 cm. long at 63 l. per hr. gave 7 gm. oil, 3 gm. tar, and 0.2 gm. C. Higher temperatures with the same gas flow favor precipitation of C. Tar and oil do not form to an appreciable extent below 900°. The tar is aromatic, naphthalene, anthracene and phenanthrene being isolated. The oils contain mostly benzene with xylene and $C_{10}H_8$. SiO_2, W, Mo, and Sn as catalysts did not favor oil yield; Fe, Cu, and graphite favored C precipitation.

Fischer, L. E. *See* abs. 1579a.

Fischer, W. *See* abs. 868.

Fischer, W. A. *See* abs. 1966.

1049. Fishel, W. P., and Wooddell, J. S. Action of Pure Carbon Monoxide Upon Iron at Elevated Temperatures. Trans. Am. Soc. Steel Treating, vol. 11, 1927, pp. 730–740; Chem. Abs., vol. 21, 1927, p. 3873.

Reaction between CO and Fe to produce Fe_3C and CO_2 has been demonstrated to obey the laws of reversible reactions.

Fisher, P. L. *See* abs. 923, 927, 929.

Fleming, H. W. *See* abs. 574.

1050. Fletcher, C. J. M., and Rollefson, G. K. Production of Free Radicals From Ethylene Oxide and the Catalysis of Other Reactions by Them. Jour. Am. Chem. Soc., vol. 58, 1936, pp. 2135–2140; Chem. Abs., vol. 31, 1937, p. 936.

When ethylene oxide is heated to 450° the chief reaction is in isomerization to AcH, but free radicals also are formed to a much greater extent than for most other organic compounds. MeOH at 465° decomposes to the extent of 24.5% in the presence of ethylene oxide, whereas the uncatalyzed reaction is inappreciable at this temperature.

1051. Fleury, M. [Manufacture of Synthetic Methanol.] Mem. poudres, vol. 24, 1931, pp. 10–48; Chem. Abs. vol. 25, 1931, p. 3310.

Describes mechanical installation and experimental chemical work on the semi-plant-scale production of MeOH from water gas and H_2 in 1922. The best catalyzers were 90% Cu, 10% ZnO, Mn and Zn chromates. High gas speed and high temperatures favored the formation of higher alcohols.

Floe, C. F. *See* abs. 2562.

Foehr, T. *See* abs. 2935.

1052. Fohlen, J. [Cracking and Catalysis.] Chim. et ind., Special No., 1932, pp. 273–277; Chem. Abs., vol. 26, 1932, p. 3357.

Decomposition of Saar coal at very high pressures and temperatures is investigated, both in the presence and absence of solvents which are not volatile at the temperatures used, and in the presence and absence of various catalysts. The problem of the industrial synthesis of liquid fuels is also discussed.

Foran, E. *See* abs. 3038.

Forestier, H. *See* abs. 479.

1053. Forestier, H., and Chaudron, G. [Points of Magnetic Transformation in the System Sesquioxide of Iron–Magnesia.] Compt. rend., vol. 181, 1925, pp. 509–511; Chem. Abs., vol. 20, 1926, p. 698.

Study of system $Fe_2O_3 \cdot MgO$ at various temperatures by dilatometry and also by magnetic susceptibility. The results show the existence of $Fe_2O_3 \cdot MgO$.

1054. ———. [Thermomagnetic Study of Some Ferrites.] Compt. rend., vol. 182, 1926, pp. 777–779; Chem. Abs., vol. 20, 1926, pp. 1939–1940.

Curves showing the change in magnetization with temp. between 0° and 600° to 900° are given for $Fe_2O_3 \cdot CrO$, $Fe_2O_3 \cdot FeO$, $Fe_2O_3 \cdot NiO$, $Fe_2O_3 \cdot MgO$, $Fe_2O_3 \cdot CaO$, $Fe_2O_3 \cdot BaO$, $Fe_2O_3 \cdot PbO$ and $Fe_2O_3 \cdot ZnO$. The mean specific susceptibilities for these ferrites for fields 0–100 gausses are given as 0.102, 0.080, 0.078, 0.054, 0.0425, 0.0099, 0.0012, and 0.00016, respectively.

1055. Forestier, H., and Guiot-Guillan, G. [A New Series of Ferromagnetic Substances; the Ferrites of the Rare Earths.] Compt. rend., vol. 230, 1950, pp. 1844–1845; Chem. Abs., vol. 44, 1950, p. 7700.

Compounds of the type $Fe_2O_3 \cdot M_2O_3$, where M is La, Pr, Nd, Sm, Er, or Y, were prepared by coprecipitation of the oxides followed by heat treatment. They are stable up to 1,000°, although in some cases decomposition occurs after prolonged heating of 1,000°. Magnetization curves were obtained. Ferromagnetic Curie points are: $Fe_2O_3 \cdot La_2O_3$, 465°; $Fe_2O_3 \cdot Pr_2O_3$ 425°; Fe_2O_3 Nd_2O_3, 300°; $Fe_2O_3 \cdot Sm_2O_3$, 300°; $Fe_2O_3 \cdot Er_2O_3$, 255°; $Fe_2O_3 \cdot Y_2O_3$, 275°.

1056. Forestier, H., and Kiehl, J. P. [Effect of Gaseous Adsorption on the Velocity of Reaction of Metallic Oxides.] Compt. rend., vol. 229, 1949, pp. 47–49; Chem. Abs., vol. 44, 1950, p. 403.

Yields of ferrite from powdered Fe_2O_3 and NiO heated in atmospheres of H_2O, CO_2, O_2, air, N_2, Ne, A, and He at 600°, 650°, and 700° plotted as isotherms against absolute temperature of liquefaction of the gases give smooth curves except for N_2, which gives a low yield. Yields decrease with particle size. The explanation advanced is that the gases are most readily adsorbed in the order named, and adsorption swells the particles till they shatter.

1057. ———. [Effect of Adsorbed Gases on the Rate of Reaction Between Metallic Oxides.] Jour. chem. phys., vol. 47, 1950, pp. 165–173; Chem. Abs., vol. 44, 1950, p. 7128.

The rate of formation of ferrite from Fe_2O_3 and NiO increases logarithmically with the partial pressure of H_2O present over the pressure range of 10^{-5}–760 mm. at 500°–700°. Extrapolation indicates 0 reaction rate at 10^{-9} mm. The order of decreasing efficiency of gases in speeding up the reaction in the temperature range 600°–700° is H_2O, CO_2, A and O_2, air, N_2, Ne, and He.

1058. Forestier, H., and Lille, R. [Variation in Catalytic Power of Ferromagnetic Substances at the Curie Point.] Compt. rend., vol. 23, 1937, pp. 204, 265–267; Brennstoff-Chem., vol. 18, 1937, p. 286; Chem. Abs., vol. 31, 1937, p. 2077.

It has been shown that the speed of inauguration of the equilibrium reaction, $2CO \rightleftharpoons CO_2+C$, in the presence of ferromagnetic metals changes whenever the catalyst Fe or Ni loses its ferromagnetism. A series of ferromagnetic oxides of the type of the ferrites, Fe_3O_4, $Fe_2O_3 \cdot SrO$ and $Fe_2O_3 \cdot NiO$, was investigated for the catalytic power on the inauguration of the water-gas equilibrium $CO_2+H_2 \rightleftharpoons CO+H_2O$ in the temperature range of their Curie points of 350°–700°. A $CO_2 : H_2$ (55 : 45) mixture was used at a velocity of 1 l./hr. The amount of H_2O formed in the reaction plotted against the temperature was used as the criterion for the catalytic efficiency. In the temperature range of the magnetic transition point, for $Fe_2O_3 \cdot SrO$ 480°, for Fe_3O_4 570°, decided maxima occurred in the curves. Three curves for $Fe_2O_3 \cdot NiO$, giving results of 3 successive tests, reveal the progressive reduction of the catalyst. In the first test a maximum in the Curie point of the Ni ferrite occurs at 595°, but in the following tests the $Fe_2O_3 \cdot NiO$ obviously decomposes with formation of Fe_3O_4 as a second maximum point is observed at about 570°. A thermomagnetic analysis confirms this. It is suggested that 3 temporary increases in catalytic power are connected with the changes at the Curie point and are due to a special mobility of some of the superficial electrons at that point.

1059. Forestier, H., and Longuet, J. [Formation of Cupric Ferrite at Low Temperature.] Compt. rend., vol. 208, 1939, pp. 1729–1730; Chem. Abs., vol. 33, 1939, p. 5764.

By precipitation of a suitable mixture of ferric and cupric salts with NaOH, a mixture of $Fe(OH)_3$ and $Cu(OH)_2$ in molecular proportions was obtained. On boiling this mixture in H_2O, ferromagnetism began to appear after ½ hr. and gradually increased, the limit being reached after about 24 hr., when it equaled that of $CuO \cdot Fe_2O_3$ heated above 400°. The Curie point was 455°. X-rays indicated that the precipitate was at first amorphous and gradually became crystalline with boiling, developing the spinel structure of $Cu(FeO_2)_2$. This is confirmed by the fact that KCN solution dissolves the Cu from the unboiled precipitate, but is without action on the ferromagnetic product. The production of $Cu(FeO_2)_2$ takes place only in the presence of H_2O and between the anhydrous oxides.

1060. Forestier, H., and Nury, G. [Variation of the Velocity of Cementation of Iron at the Temperature of the Curie Point.] Compt. rend., vol. 227, 1948, pp. 280–282; Chem. Abs., vol. 43, 1949, p. 472.

Velocity of cementation of Fe at temperatures 600°–800° was followed by 2 methods: Variation of electric resistance of wires and hardness of polished faces of cubes. The velocity was a maximum at the Curie point, about 775°.

1061. ———. [Speeds of Reaction in the Vicinity of Magnetic Transformation Points. Application to the Cementation of Iron.] Bull. soc. chim. France, 1949, D, pp. 193–196; Chem. Abs., vol. 43, 1949, p. 6018.

Rate of formation of ferrite from NiO and Fe_2O_3 is studied near the Curie point. Maxima in the % product are observed at 590° and 675°, the Curie points of ferrite and Fe_2O_3, respectively. These maxima are attenuated as the time of heating at 450°–800° is extended from 2 min. to 24 hr. The conclusion is that the magnetic transformation acts essentially on the chemical reaction and not on the speed of diffusion. The cementation of Fe in illuminating gas and in CO is also studied by measuring the variation of electric resistance of an Fe wire and the variation of surface hardness of an Fe cube. Pronounced maxima are observed at the Curie temperature of Fe. Similar results are indicated for the nitridization of Fe.

1062. Forestier, H., Haasser, C., and Longuet-Escard, J. [Reaction in the Solid State at Low Temperature. Influence of the State of the Surface and of the Water Vapor Adsorbed.] Bull. soc. chim. France, 1949, D, pp. 146–152; Chem. Abs., vol. 43, 1949, p. 6059.

Magnetic detection of ferrites is used to study the rate of reaction between solid Fe_2O_3 and oxides of Ni, Pb, and Mg at temperatures low enough for diffusion to be neglected. For Ni and Pb, reaction can be detected at 200°; for Mg, only above 400°. Starting mixtures are prepared in 3 ways: (*A*) Coprecipitation followed by drying at 100° in vacuo, (*B*) separate precipitation and drying followed by mixing, (*C*) separate precipitation and drying at 750° followed by grinding. The rate and extent of reaction at a given temperature (up to 700°) are $(A) > (B) > (C)$. The presence of water vapor even in trace amounts considerably increases the rate of reaction for (*A*) and (*B*) and has a small effect for (*C*). X-ray analyses indicate that with Ni (*A*) is amorphous but (*C*) is well-crystallized; with Mg (*A*) and (*B*) show $Mg(OH)_2$, but (*C*) shows MgO; with Pb (*A*) is amorphous, but (*B*) and (*C*) show the crystalline structure of PbO. With NiO–Fe_2O_3 mixture (*B*) at 500°, grinding during the interval of rising temperature results in a slower reaction during the 1st 1½ hr. at constant temperature, but a faster reaction thereafter. Compression of the initial NiO–Fe_2O_3 mixture (*B*) gives a minimum in the % product-pressure curve at about 1,500 kg./cm.^{2} Mixture (*C*) shows no minimum. The data are explained in terms of the number of contact points and the effect of adsorbed water vapor on the surface crystal lattice.

Foroud, A. K. *See* abs. 162.

Forrer, R. *See* abs. 3639, 3640, 3641, 3642.

Forrest, H. O. *See* abs. 1365.

1063. Fortune. Coming: Ersatz Gasoline. Vol. 31, 1945, pp. 200, 203.

Our present crude petroleum reserves have dwindled to about a 14-yr. supply at the present rate of consumption, assuming that no new oil is found and that all of the present reserve can be brought above ground. To supplement that, we have other raw materials from which liquid fuels can be made: Natural gas about equal to the proved petroleum reserves, oil shale sufficient to maintain the normal rate of oil production for 65 yr., tar sands which contain enough oil for gasoline for 100 yr., and, finally, vast coal reserves, enough to supply liquid fuel by the Bergius and Fischer synthetic processes for 1,000 yr. or more. Some conservation-minded experts believe that natural gas should be used as such, since gas loses about half its heat content in being converted into gasoline. Therefore, the Bureau of Mines, in its study of the production of liquid fuels, is turning down natural gas and giving its attention to the production of gasoline and fuel oils from oil shale and from coal by means of the Fischer and Bergius processes. Economically, it is believed that gasoline made by the Fischer process is competitive with gasoline made from crude petroleum, and 2 companies are now ready to construct commercial Fischer plants. However, it is believed that success may not be too rapid, since the transfer of the process from laboratory and pilot-plant stage is sure to be difficult, obsolescence will be rapid, the after-war market for gasoline may be bad, with 7,000,000 cars off the road, and the supply of natural gas is not too secure, with 75% of it already earmarked for other industrial and domestic uses and being consumed at a rate that will exhaust present proved reserves in about 30 yr.

1064. ———. Synthetics: The Great Oil Reserve. Vol. 37, No. 5, 1948, pp. 110–115, 153–154, 156, 158, 160, 162, 164, 166.

Review of developments in setting up a synthetic fuel industry involving the utilization of our natural gas, coal, and shale resources. The economic possibilities of such a program is discussed quite thoroughly. It is concluded that the immediate creation of a huge synthetic fuel industry at enormous cost would disrupt our national economy. The best solution seems to be a combination of vigorous domestic exploration of our energy resources pointing toward a balanced national policy for making the most of them, a stockpiling of national oil products, and the creation of a more manageable synthetic program subsidized by the military, which could supply plans and improvements for quick expansion in an emergency.

1065. Foster, A. L. Fischer-Tropsch Synthesis May Prove a Major Oil-Refining Process. I. The Reaction, Its Mechanism and Its Products. Oil Gas Jour., vol. 43, No. 15, 1944, pp. 99, 101, 106, 109; Chem. Abs., vol. 39, 1945, p. 3895.

Synthol theory of Elvin and Nash and the carbide theory of Fischer are discussed. The nature of the products is discussed in general terms, with reference to the influence of operating conditions and of the nature of the catalyst used.

1066. ———. Fischer-Tropsch Synthesis May Prove a Major Oil-Refining Process. II. Methods of Operation. Oil Gas Jour., vol. 43, No. 17, 1944, pp. 46–49; Chem. Abs., vol. 39, 1945, p. 3895.

For a given product to be obtained in satisfactory yield, good temperature control of the reaction is essential, and to avoid poisoning of the catalyst, S should be removed from the reactants. Various methods for the production of high-antiknock hydrocarbons are discussed. The nature of the products varies widely with temperature, pressure, and nature of catalyst used.

1067. ———. Fischer-Tropsch Synthesis May Prove a Major Oil-Refining Process. III. Catalysts and Their Preparation. Oil Gas Jour., vol. 43, No. 18, 1944, pp. 66, 69, 91; Chem. Abs., vol. 39, 1945, p. 3895.

Usual main constituent of the catalyst is 1 or more group VIII metals mixed, if desired, with 1 or more of a wide range of promoters. The catalyst is usually prepared by reduction of a salt or an oxide of the metal, and may be supported on any one of a number of suitable materials—for example, kieselguhr. The precise methods used in preparing the catalyst are critical, since its physical state is as important as its chemical nature.

1068. ———. Chemical Utilization of Natural Gas Limited Only by Commercial Demand. Oil Gas Jour., vol. 44, No. 52, 1946, pp. 83, 84, 91.

Reactions employed to convert natural gases into more useful commercial products include alkylation, polymerization, isomerization, dehydrogenation, condensation, and synthesis. The combination of reactions comprising the Fischer-Tropsch process is referred to as the most versatile synthetic system that has been developed for use on petroleum and natural-gas hydrocarbons. The products range from the lightest oxidation products, such as alcohols, to the heaviest paraffin waxes with molecular weights above 2,000. In addition a long list of aldehydes, ketones, acids, ethers, and other oxygenated products are made. The nature of the hydrocarbons synthesized ranges from the highly paraffinic straight chain products almost entirely free of isomers or olefins into the relatively high octane number products consisting mainly of isomeric hydrocarbons in the gasoline range and heavier, higher-boiling materials of the less paraffinic types. Some 4–6 gal. of gasoline per 1,000 cu. ft. of raw gas can be made. For each bbl. of gasoline produced, there are required 1,360 lb. of coal, or 11,950 cu. ft. of CH_4 (modern designed plants, 10,450 cu. ft.) with a percentage fuel value conversion of 31, 42.5 (48.3), respectively. Comparative yields of products by atmospheric and medium-pressure processes are charted.

1069. ———. Postwar Refinery Operations Capitalize on Skills Developed During Emergency. Fischer-Tropsch Developments. Oil Gas Jour., vol. 45, No. 12, 1946, pp. 165, 216.

Progress in this field has been in developing and perfecting catalysts, equipment, and procedures to improve yields and properties and reduce costs. It is tentatively estimated that gasoline can be produced for $0.0525 per gal., including interest, depreciation and amortization. As regards catalysts, it appears that the sintered Fe type is being favored, with operation by the fluid principle. The technical feasibility of the Fischer process is already demonstrated but its economic practicability is yet to be proved. A crude price ceiling of $2.00 per bbl. has been mentioned as the minimum with which the synthetic process could economically compete.

1070. ———. Hypersorption. Oil Gas Jour., vol. 47, No. 15, 1948, pp. 90, 93, 94, 97, 99, 100.

This process, developed by Union Oil Co. of California, employs the principle of selective adsorption of hydrocarbons by a moving bed of activated C particles, with subsequent removal of the adsorbed hydrocarbons by heat and steam. It has been applied especially to recovery of C_2H_4 and the like from natural gas and cracked gas where high recoveries and high concentrations of the products are desired. The Dow Chemical Co. has a unit at Midland, Mich., designed to process a maximum of 1,800,000 cu. ft. of cracked gases per day. It will circulate up to 32,000 lb. of C per hr. and will strip the C at 500° F. or higher. From a feed containing about 6% C_2H_4, 98–99% was recovered in a CO_2-free purity of about 95%. In separating H_2 from a charge containing 52.2% H_2, 43.5% CH_4, and small amounts of C_2 and C_3, the discharge has showed 100% H_2, with 91% CH_4 and virtually no H_2 in the make gas. Operations to concentrate C_3H_8 show results of 99.2% of C_3H_8 in the make gas from charge containing 28.8% C_3.

1071. ———. Merger of Synthetics Programs. Oil Gas Jour., vol. 46, No. 44, 1948, p. 42.

Cities Service Oil Co. and M. W. Kellogg Co. have merged their synthetic fuel research programs and are prepared to license synthetic fuel plants for operation of the process. Cities Service Co. has been interested for several years in the chemistry and technology of natural gas and is one of the largest producers and controls one of the largest gas reserves in the United States. Research is now being concentrated on the isolation purification of the byproduct chemicals obtained during the process, and the reconversion of the oxygenated products to hydrocarbons. It is stated that the cost of producing a synthetic crude oil is comparable at present to the price of crude oil.

1072. ———. Texaco Now Licensing Process for Synthetic Fuel Production. Oil Gas Jour., vol. 46, No. 41, 1948, p. 68.

Hydrocol process for making synthetic gasoline and other products from natural gas has been tested commercially in a 120-bbl.-per-day pilot plant of the Texas Company at Montebello, Calif., and is being offered for general license. It is estimated that enough natural gas is available in the United States to support 50 Hydrocol plants producing a total of 350,000 bbl. gasoline per day. It is estimated also that the overall cost for present-day American plants will be only about ⅓ that of the German plants. The Fe catalyst used on the fluidized principle has a life of 500 hr. and costs $0.05–$0.10 per lb.

1073. ———. Synthetic Fuels Plant in Shakedown Stage. Petrol. Eng., vol. 23, No. 2, 1951, pp. C29–C30.

Synthetic fuels plant of Carthage Hydrocol and the Stanolind Oil & Gas Co. plant adjacent thereto are being made ready for initial operation. The Hydrocol plant will produce gasoline and oil from natural gas by a modified Fischer-Tropsch process, and the Stanolind plant will work up the dilute, liquid byproducts, such as alcohols, aldehydes, acids, ketones, etc., for delivery to the United States Industrial Chemicals for use as raw materials or intermediates in the manufacture of chemicals. The main steps in the process are pointed out.

1073a. ———. Status of Synthetic Fuels. Petrol. Eng., vol. 24, No. 10, Sept. 1952, pp. C3–C4.

Brief review of economic studies and technological advances.

1074. Foster, J. F. Investigation of a Continuous Process for the Production of Water Gas From Pulverized Coal. Symposium on Production of Synthesis Gas, 112th Meeting American Chemical Society, September 1947, pp. 137–150; Ind. Eng. Chem., vol. 40, 1938, pp. 586–592; Chem. Abs., vol. 42, 1948, p. 4328.

Investigation was made of the feasibility of producing water gas by a continuous method by reacting steam and pulverized coal in a vertical, externally heated alloy tube, 25–12 Cr–Ni, 11 ft. long and 5 in. and 8¼ in. inside diameter, respectively, suspended in and passing through the furnace and heated externally by gas burners to approximately 2,100° and 1,850° F. Only noncoking coals were used successfully at varying feed rates. The rate of production of water gas was found to depend on temperature, rate of fuel feed, rate of stream supply, tube dimension, and chemical reactivity of the fuel. An empirical equation has been developed describing the effect of these variables on gas production. A new constant, called the gasification constant, is shown for measuring the inherent activity of a solid fuel toward reaction with steam. It is useful for comparing on a common basis the gasification characteristics of different fuels at 1 temperature or 1 fuel at different temperatures since it virtually eliminates the effect of different variables on the volume of gas produced. Use of the equation permits an estimate of the capacity of equipment of commercial size for the production of water gas. Estimates of the investment of the larger equipment indicate that these costs are sufficiently higher than those of modern conventional water-gas generators of equivalent capacity to discourage commercial application of the process under present economic conditions.

1075. Foulon, A. How Germany Is Synthesizing Soap Fats. Mfg. Perfumer, vol. 4, 1939, pp. 150–151; Chem. Abs., vol. 33, 1939, p. 9026.

Brief account of fatty acid synthesis by oxidation of paraffin wax and treatment of the oxidation product.

Fox, R. E. *See* abs. 2060.

1076. Foxwell, G. E. Fuel Utilization. Jour. Inst. Fuel, Wartime Bull., vol. 19, 1945, pp. 64–71, 81; Engineering, vol. 160, 1945, pp. 502–503.

Paper presented to the Scottish Section of the Institute of Fuel and the National Smoke Abatement Society gives full report of the Nonparty Technical Commission. For the part relating to the chemical derivatives of coal and the Fischer-Tropsch process (*see* abs. 2649).

1077. Fracasso, G. [Table for Equilibrium in the Synthetic Preparation of Methanol.] Industria chimica, vol. 9, 1934, pp. 293–299; Chem. Abs., vol. 28, 1934, p. 3972.

Equilibrium of the equations $CO+H_2\rightleftharpoons H_2CO+H_2\rightleftharpoons$ MeOH is calculated form the gas law $K=P_M/p_{CO}p^2_{H_2}$, p_M, p_{CO}, p_H being the partial pressures of MeOH, CO and H_2, respectively. Values of K cited in the literature are summarized, and a nomograph of the equilibrium conditions is constructed.

Franchetti, P. *See* abs. 2554, 2555, 2556, 2557.

1078. Francis, A. W. Free Energies of Some Alcohols. Ind. Eng. Chem., vol. 20, 1928, pp. 283–284.

Equations have been derived for the free energies of formation of 9 alcohols. These have been simplified to linear equations for the range 227°–427°. A general equation for normal alcohols has been derived, and this has been compared with that for olefins to find conditions for dehydration or hydration of the olefins; and with that for CO to find conditions for synthesis.

1079. ———. Free Energies of Some Hydrocarbons. Ind. Eng. Chem., vol. 20, 1928, pp. 277–282; Chem. Abs., vol. 22, 1928, p. 1131.

From equations derived for the free energies of formation of CH_4, C_2H_6, octane, C_2H_4, C_2H_2, C_6H_6, PhMe, $C_{10}H_8$ and cyclohexane as functions of temperature it is shown that production of higher-paraffin hydrocarbons from lower ones is impossible, except with simultaneous production of still lower ones in at least equivalent amounts. The catalytic formation of C_2H_4 in more than traces is impossible. The direct removal of H from a paraffin to form an olefin with the same number of C atoms is possible only at high temperatures and to a very limited extent. Synthesis of gasoline from water gas can take place only below about 450°. Isomerization of olefins to naphthenes require temperatures below about 430°, while the production of aromatics requires 550°–900°. In the Fischer synthesis of gasoline $8CO+17H_2\rightarrow C_8H_{18}+8H_2O$; $\Delta F=-338740+479.4T$, which is negative up to 700° K. or 427° C. The operating temperature for gasoline is 275°–300°. Higher temperatures give lower hydrocarbons, especially CH_4, as should be expected.

1080. Francis, A. W., and Kleinschmidt, R. V. Applications of Thermodynamics to Chemical Reactions of Petroleum Products. Proc. Am. Petrol. Inst., 10th Ann. Meeting, vol. 11, sec. III, 1930, pp. 93–99; Chem. Abs., vol. 24, 1930, p. 2369.

It is shown that, per volume of water gas reacted, considering H_2 and CO as equivalent, formation of CO_2 is accompanied by the largest free-energy decrease, and of H_2O by the next-largest decrease. Of the hydrocarbons, CH_4 is formed with the largest free-energy decrease/volume of water gas reacted. MeOH formation is accompanied by the smallest decrease. However, formation of MeOH is accompanied by a larger decrease in volume than the formation of hydrocarbons from water gas, so that pressure may be used to direct the reaction to MeOH, as is done industrially in the presence of mixed oxide type catalysts. Although the most pronounced effect of pressure in changing the character of the product from hydrocarbons to O-containing compounds may be due to a shift in the equilibrium concentrations of the components, changes in specific reaction rates of the various reactions involved may be accountable.

1081. Frank, F. [Technical and Economic Importance of Liquid Fuels.] Wärme, vol 54. 1931, pp. 438–441; Chem. Abs., vol. 25, 1931, p. 4380.

Application of various liquid fuels for motor and industrial use and for heating purposes is discussed. and reference is made to gaseous fuels and the domestic oil industry. Fuels for light- and heavy-oil motors, natural and synthetic benzine, benzene, spirits and fuel oil are considered.

Frank, J. C. *See* abs. 1708.

1081. Frankenburg, W. G. Adsorption of Hydrogen on Tungsten. I. Jour. Am. Chem. Soc., vol. 66, 1944, pp. 1827–1828; Chem. Abs., vol. 39, 1945, p. 451.

Data are given for the adsorption of H_2 on metallic W at equilibrium pressures between 1×10^{-5} and 30 mm. and at temperatures from −194° to 750°.

Frankenburger, W. *See* abs. 224a.

1082. Frankfurter Zeitung. [New Process for Producing Diesel Oil.] April 1939.

High-class diesel fuel is being made in Germany by blending coal oils from the carbonization of coal with high-boiling fractions of the product of the Fischer synthesis. A new blending plant is being operated at Homberg by the Rheinpreussen Co. The blends now on the market are characterized by a high degree of ignitibility coupled with a smokeless exhaust and are considered to be superior to mineral-oil products.

Frantzuz, E. *See* abs. 2774.

Franz, H. *See* abs. 3058, 3060.

1083. Frazer, J. C. W. Eighth Report of the Committee on Contact Catalysis. Jour. Phys. Chem., vol. 34, 1930, pp. 2129–2179; Brennstoff-Chem., vol. 12, 1931, pp. 33–34; Chem. Abs., vol. 24, 1930, p. 5584.

General survey of the field, with a review of recent developments is given. Special organic reactions, such as the synthesis of MeOH and the higher alcohols, the synthesis of petroleum by the Fischer-Tropsch process, and the hydrogenation of coal, as well as general hydrogenation and oxidation reactions, have received extended treatment.

1084. ———. Catalytic Oxidation of Carbon Monoxide. Jour. Phys. Chem. vol. 35, 1931, pp. 405–411; Chem. Abs., vol. 25, 1931, p. 1432.

Carefully purified, finely divided MnO_2, Co_2O_3, and Ni_2O_3 are extremely active catalysts for the union of CO and O_2 at temperatures as low as 0°. Extreme purity, not the presence of promoters, is important for catalytic activity. Impurities may be removed by electrolysis of an aqueous suspension of the oxides. None of 17 other unnamed oxides studied was effective. The 3 active oxides differ from the others in 1 significant particular, namely, their composition is indefinite. By an adsorption apparatus it was shown that the O_2 pressure in equilibrium with a sample of one of these oxides depends on the composition of the oxide. Condensation of water vapor within the pores of these oxides destroys their catalytic activity. Extreme drying does not destroy the activity.

1085. Frei, —. Catalytic Cracking of Products of the Fischer-Tropsch Synthesis Over Silicon–Aluminum Catalysts. TOM Reel 170, July 2, 1941, frames 410–414.

Low-molecular products are obtained on middle-oil fractions, boiling 210°–340°, while no cracking is possible on the heavy gasoline fractions. The yields and composition of end products are compared in charts. The heavy gasoline fraction can be converted into motor gasolines.

Freiss, W. *See* abs. 1991.

Fremon, G. H. *See* abs. 2178.

1086. Freund, M. Properties of Natural and Synthetic Paraffinic Lubricating Oils. Petroleum (London), vol. 33, No. 48, 1937, pp. 1–5; British Chem. Abs., 1938, B, p. 131.

Three groups of products of high-pressure hydrogenation, solvent extraction, chemical synthesis (Fischer process), and conventional acid-earth refining were examined regarding properties dependent on mean molecular weight and H content. Each group consisted of oils of identical refractive index at 50°. The generalization connecting *d* with these properties holds satisfactorily, except for synthetic oils, which behave somewhat differently from other types.

1086a. ———. [Manufacture of Synthetic Lubricants by the Fischer-Tropsch and Other Processes.] Magyar Kém. Lapja, vol. 5, 1950, pp. 368–371.

Summary.

1087. Fricke, R., and Ackermann, P. [Heat Content and Lattice Structure of Active Ferric Oxide.] Ztschr. Elektrochem., vol. 40, 1934, pp. 630–640; Chem. Abs., vol. 29, 1935, p. 33.

The lower the temperature of dehydration of synthetic microcrystalline α-FeOOH, the greater is the energy content of the resulting α-Fe_2O_3; the energy differences as shown by heats of solution may reach 5 kcal. per mol. Fe_2O_3. Quantitative photometric measurements of x-ray powder photographs show imperfect lattice formation of the low-temperature Fe_2O_3, rather than differences in particle size or in lattice dimensions relative to the high-temperature Fe_2O_3. Tempering at 220° increases the lattice perfection of low-temperature Fe_2O_3 and restores its energy content to normal.

1088. Fricke, R., Walter, K., and Lohrer, W. [Effect of the Physical State of the Solid Reactants on the Equilibrium Fe/Fe_3O_4 with H_2O/H_2.] Ztschr. Elektrochem., vol. 47, 1941, pp. 487–500; Chem. Abs., vol. 36, 1942, p. 4010.

Below 560°, Fe reacts with steam according to the binary equilibrium, $3Fe+4H_2O \rightleftharpoons Fe_3O_4+4H_2$; above 570°, FeO is first formed, and from this Fe_3O_4. The equilibrium was measured at a constant steam pressure, so that the only variable was the pressure of the H_2. Calorimetric data and specific heats indicate that at 525° the heat of reaction is greater for active Fe than for ordinary Fe by about 22.6 kcal. An x-ray examination of active Fe at 450° indicated an average particle size of 275 Å., and for inactive Fe 470 Å. The increase in the heat of reaction when active Fe is used is due to the increased heat content. Owing to large differences in the surface of the Fe particles, x-ray results are not sufficient to account for the large differences in the heat of reaction. This may be due to the fact that x-ray values are always average values, whereas only the more active particles are involved in equilibria.

1089. ———. [Effect of the Physical State of the Solid Reactants on the Equilibrium Fe/Fe_3O_4 with H_2O/H_2. Addendum.] Ztschr. Elektrochem., vol. 47, 1941, p. 811; Chem. Abs., vol. 36, 1942, p. 4010.

Instead of the value of 265.4 kcal. given in abs. 1088, the authors propose the later value of 266.76±0.22 kcal. by Roth and Wienert (abs. 2909) for the heat of reaction.

Friedel, R. A. *See* abs. 43, 43a, 49, 3645, 3646, 3651, 3656b, 3656c.

1090. Friedel, R. A., and Anderson, R. B. Composition of Synthetic Liquid Fuels. I. Product Distribution and Analysis of C_5–C_8 Paraffin Isomers From Cobalt Catalyst. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1212–1215, 2307.

Distribution of Fischer-Tropsch synthesis products has been given C_1–C_{20} for precipitated Co catalysts, using H_2 : CO=2 : 1 at atmospheric pressure and 190°. Quantitative analysis of C_5–C_8 paraffin isomers by mass spectrometry showed only the presence of monomethyl isomers. The predominant components, the straight-chain isomers, decreased with increasing molecular weight. Approximate analyses of olefins showed that internal doublebond olefins were the major constituents. Preliminary results on Fe-catalyst products also are reported.

1091. Friedel, R. A., and Sharkey, A. G. Analysis of Oxygenated Compounds by Mass Spectrometer. Anal. Chem., vol. 23, No. 4, 1951, p. 677.

Abstract of paper presented at the 2d Pittsburgh Conference on Analytical and Applied Spectroscopy. A liquid introduction system has been adapted for rapid vaporization of 0.0005-cc. samples of liquids into a mass-spectrometer vacuum system, with a reproducibility of about 1%. No sealing gaskets are required. Analysis of oxygenated compounds includes determination on dilute aqueous solutions of alcohol, ketone, and acid mixtures. Determinations on gas samples containing alcohols, aldehydes, and ketones from the oxidation of light hydrocarbons have been carried out. These mixtures are complicated by the expected secondary reactions between aldehydes and alcohols to produce acetals.

1091a. ———. Mass Spectrometry in Synthetic Fuels. Consolidated Eng. Corp. Recordings, vol. 5, No. 3, Sept. 1951, pp. 1, 5, and 10.

Friederichs, H. *See* abs. 167.

1092. Friedwald, M. [Status of the Synthesis of Hydrocarbons.] Rev. combust. liquides, vol. 12, 1934, pp. 277–281.

Discusses work of Fischer.

1093. ———. [Preparation of Liquid Motor Fuel From Carbon Monoxide and Hydrogen.] Rev. pétrolifère No. 634, 1935, pp. 733–735; Chem. Zentralb., 1935, II, p. 1290; Chem. Abs., vol. 29, 1935, p. 5626.

Results with a semi-large-scale plant are described; factors influencing yields, etc., are discussed as follows: Increase of pressure favors synthol production; of H_2 favors CH_4; decrease of H_2 favors olefins; increase of temperature favors CH_4 and C; catalysts increase the degree of saturation of the product in the order Fe, Co, Ni; presence of CO_2 is without influence; increase of life of catalyst gives an increase of light fraction and a decrease in oil content.

1094. ———. [Problems of Artificial Motor Fuels and Substitutes.] Ann. combust. liquides. vol. 13, 1935, pp. 247–251; Chem. Zentralb, 1936, I, p. 689.

General review of production of fuels by high- and low-temperature carbonization, pressure hydrogenation, and the Fischer-Tropsch process.

1094a. Fritsche, W. Water-Gas Equilibrium and Its Relation to Practical Gasification Processes. Brennstoff-Chem., vol. 3, 1950, pp. 337–350. Chem. Abs., vol. 45, 1951, p. 1,749.

1095. Frolich, P. K. Role of Catalysts in High-Pressure Synthesis From Water Gas. Jour. Soc. Chem. Ind., vol. 47, 1928, pp. 173–179T; Chem. Abs., vol. 22, 1928, p. 3282.

High-pressure synthesis of NH_3 and of synthol is briefly discussed. The latter process is considered to be prohibitive from a commercial standpoint because of the complexity of the products obtained. These 2 applications of high-pressure technic have demonstrated the possibility of synthesizing the entire aliphatic range of compounds from the cheapest grade of coal and have stressed the necessity of bringing the reactions under control so as to obtain (1) 1 compound, (2) a limited number of single compounds or (3) a mixture of related compounds. The synthesis of any aliphatic compound is possible by studying intensively temperature, pressure and specific catalysts. The synthesis of alcohols by oxide catalysts is outlined, and it is shown that there is a very close relation between the decomposition and synthesis of CH_3OH.

1096. ———. Use of Metallic Oxides as Catalysts in Certain Organic Chemical Processes. Trans. Electrochem. Soc., vol. 71, 1937, pp. 313–331; Chem. Abs., vol. 31, 1937, p. 3372.

Specific illustrations indicate their extreme usefulness in the organic field. Their high degree of selectivity and their resistance to the ordinary catalyst poisons are outstanding characteristics. The results obtained in the studies of MeOH and higher alcohols are helpful in throwing light on the catalytic and general physical properties of this class of oxides. It was found that a definite relation exists between the synthesis of the alcohol from CO and H_2 at high pressure and its decomposition over the same catalyst combinations at atmospheric pressure. So close was the agreement between the two sets of observations that the simple and inexpensive decomposition method could be used for evaluating the usefulness of catalysts for the high pressure synthesis. It was also found that in the decomposition of MeOH, any mixture of 2 oxides (ZnO–CuO, ZnO–Cr_2O_3) had a synergistic effect, the addition of 3 mol. % ZnO to CuO increasing the rate approximately 3 times.

Frolich, P. K. *See* abs. 1101, 1102, 2109, 2485.

Frolich, P. K., and Cryder, D. S. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. VI. Investigation of the Mechanism of Formation of Alcohols Higher Than Methanol. *See* abs. 1103.

1097. Frolich, P. K., and Lewis, W. K. Synthesis of Alcohols Higher Than Methanol From Carbon Monoxide and Hydrogen. Ind. Eng. Chem., vol. 20, 1928, pp. 354–359; Chem. Abs., vol. 22, 1928, p. 1755.

Steel or Cr-steel turnings impregnated with KOH was unsatisfactory, the loss as gaseous products varying from 30–70%. A low-Cr steel with a minimum of added alkali appeared the most effective. The highest oil yield obtained was 13.4%, and increase of oil yield was associated with increase of gas losses. In combination with a MeOH catalyst, gas losses were less, but only traces of oil were obtained, the product being a mixture of MeOH and higher alcohols. Metallic oxide catalysts, such as a mixture of ZnO, Cr_2O_3, and $Ba(OH)_2$ on Cu, which yield MeOH at 300°–350°, produced higher alcohols at 450°–500°. The best yield recorded, however, was 13.9%, chiefly PrOH. The loss was somewhat less than with Fe-alkali catalysts and the product was largely alcoholic in place of the complex mixture of alcohols, aldehydes, etc. obtained in the other case.

Frolich, P. K., Davidson, R. L., and Fenske, M. R. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. III. X-Ray Examination of Methyl Alcohol Catalysts Composed of Copper and Zinc. *See* abs. 1100.

1098. Frolich, P. K., Fenske, M. R., and Quiggle, D. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. I. Decomposition of Methanol by Catalysts Composed of Copper and Zinc. Ind. Eng. Chem., vol. 20, 1928, pp. 694–698; Chem. Abs., vol. 22, 1928, p. 3338.

Study of the catalytic decomposition of CH_3OH at 360° and 1 atm., with mixtures of ZnO and CuO in varying proportions, indicates that the maximum decomposition and formation of CO occur when the ZnO is present in excess. At 40–50 mol. % ZnO, the molecules CO formed per mol. CH_3OH increase about 350%. The addition of a small amount of ZnO to CuO very markedly increases the decomposition of CH_3OH. A catalyst consisting of 3 mols. % ZnO and 97% CuO decomposes 26% of the CH_3OH, while pure Cu decomposes only 9% under similar experimental conditions. A mixture containing 98.6 mols. % ZnO and 1.4 mols. % CuO decomposes 41% of the CH_3OH, whereas pure ZnO decomposes 33% under similar experimental conditions. Cu promoted with ZnO favors formation of $HCOOCH_3$, and CO formation is favored by ZnO promoted with Cu.

1099. Frolich, P. K., Fenske, M. R., Taylor, P. S., and Southwick, C. A. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. II. Synthesis of Methanol With Catalysts Composed of Copper and Zinc. Ind. Eng. Chem., vol. 20, 1928, pp. 1327–1330; British Chem. Abs., 1929, A, p. 153; Chem. Abs., vol. 23, 1929, p. 816.

Data on the decomposition of MeOH by CuO–ZnO catalysts at atmospheric pressure have been correlated with experiments on MeOH synthesis at 204 atm., the same catalysts being used. The curves for "% of decomposed MeOH appearing as CO" vs. "composition of catalyst" are of the same shape as those representing "% of CO converted to MeOH" plotted against the same abscissas. Conclusion: The atmospheric pressure decomposition method of testing is eminently fitted for studies of the activity of catalysts for the MeOH synthesis from water gas at high pressure.

1100. Frolich, P. K., Davidson, R. L., and Fenske, M. R. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. III. X-Ray Examination of Methyl Alcohol Catalysts Composed of Copper and Zinc. Ind. Eng. Chem., vol. 21, 1929, pp. 109–111; Chem. Age, vol. 20, 1929, p. 187; British Chem. Abs., 1929, A, p. 406; Chem. Abs., vol. 23, 1929, p. 1342.

Zn oxide is partly reducible at 200°–220° in a stream of MeOH vapor, particularly when in admixture with Cu oxide. The exothermic reduction of the latter oxide may furnish the necessary energy for the partial reduction of the Zn oxide. An attempt has been made to ascertain by X-ray examination if the Zn oxide is reduced to the metallic state. It has not been possible to prove the presence of metallic Zn, although there are indications that it is present. The complete series of Zn oxide—Cu catalysts studied (from pure oxide to pure Cu) all possess the characteristic crystal structure of the 2 components. The cell-unit sizes of both Cu and Zn oxide are markedly influenced by the presence of the other constituent. The selective activity of these catalysts appears to be related in some way to the distances separating the atoms of their constituents.

1101. Cryder, D. S., and Frolich, P. K. Catalyst for the Formation of Alcohols From Carbon Monoxide and Hydrogen. IV. Decomposition and Synthesis of Methanol by Catalysts Composed of Zinc and Chromium Oxides. Ind. Eng. Chem., vol. 21, 1929, pp. 867–871; British Chem. Abs., 1929, B, p. 934; Chem. Abs., vol. 23, 1929, p. 5157.

Excess of Cr_2O_3 results in the formation of appreciable amounts of CO_2 and unsaturated hydrocarbons, while with an excess of ZnO in the catalyst, CO and H_2 are the main products formed, a sharp maximum occurring at a catalyst composition of approximately $Zn_{78}Cr_{22}$. The relatively constant % of HCHO formed indicates its intermediate formation in the decomposition of MeOH. Reversing the reaction, it is found that the production of MeOH from CO and H_2 parallels the formation of CO and H_2 in the decomposition experiments. The results demonstrate the suitability of the decomposition method as a criterion in the selection of catalysts for the high-pressure synthesis of MeOH. 7 graphs are shown.

1102. Fenske, M. R., and Frolich, P. K. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. V. Decomposition and Synthesis of Methanol With a Zinc-Copper-Chromium Oxide Catalyst. Ind. Eng. Chem. vol. 21, 1929, pp. 1052–1055; British Chem. Abs. 1930, B, p. 49; Chem. Abs., vol. 24, 1930, p. 334.

Catalyst composed of the oxides of Cu, Zn, and Cr in the molal ratio of 49 : 43 : 8 has considerably higher activity for both the decomposition and the synthesis of MeOH than any of the binary systems Cu–Zn and Cr–Zn discussed in previous papers. With a space velocity of 25 cc. of gaseous MeOH per hr. per cc. of catalyst the catalyst showed marked activity even at 220° while at 285°, 90% of the MeOH was decomposed. At temperatures above 250° the decomposition was almost entirely into CO (33%) and H_2 (67%). Activity of the catalyst decreases gradually, but it can be restored by oxidation and subsequent reduction with MeOH vapor. The reduction of the catalyst with MeOH vapor is apparently preceded by decomposition of the MeOH into CO and H_2, and the reduction of the catalyst is due to the CO. In the synthesis of MeOH from CO and H_2 under high pressures, the conversions are high for this catalyst, and it is active at low temperatures.

1103. Frolich, P. K., and Cryder, D. S. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. VI. Investigation of the Mechanism of Formation of Alcohols Higher Than Methanol. Ind. Eng. Chem., vol. 22, 1930, pp. 1051–1057; Chem. Abs., vol. 24, 1930, p. 5717.

Frolich and Cryder continue their study of the high-pressure synthesis of alcohols from mixtures of CO and H_2 (abs. 1100). The mechanism of formation of alcohols higher than MeOH has been determined by studying the behavior of the individual compounds that might form as intermediates. With MeOH as an intermediate product the higher alcohols are formed by successive condensation of lower ones. The initial condensation of MeOH to EtOH controls the overall rate of this stepwise process: $2MeOH \rightarrow EtOH + H_2O$. The ease with which further condensation takes place accounts for the small amount of EtOH in the product. CO in excess aids in the formation of higher alcohols because it acts on the water vapor and removes it from the surface of the catalyst: $H_2O + CO \rightarrow CO_2 + H_2$. This reaction explains the presence of large amounts of CO_2 in the higher alcohol synthesis. Any acids formed are found as esters and these appear to be produced directly by polymerization of aldehydes rather than by the intermediate production of acids by addition of CO to MeOH.

1103a. Nussbaum, Jr., R., and Frolich, P. K. Catalysts for Formation of Alcohol From Carbon Monoxide and Hydrogen. VII. Studies of Reduction of Methanol Catalyst. Ind. Eng. Chem., vol. 23, 1931, pp. 1386–1389; Chem. Abs., vol. 26, 1932, p. 1503.

Samples of a MeOH catalyst containing 58.3 mol. % ZnO and 41.7 mol. % CuO were reduced at progressively higher temperatures. The activity as measured by the decomposition of MeOH slowly increased as the temperature of reduction rose until a certain point was reached after which any rise in temperature caused a rapid decline in the effectiveness of the catalyst. The percentage of CO in the decomposition products followed the catalytic activity, whereas the percentage of HCHO followed a curve which was the reverse of the activity of the catalyst. The catalyst was found by X-ray examination to be crystalline for all temperatures of reduction. The CuO was found to be reduced to Cu having a unit cell size of 3.634 Å. U. This corresponds to α-brass containing 13% Zn. A shorter period of reduction was found partly to offset the lessened catalytic activity due to sintering. Reoxidation of the catalyst stimulated its activity temporarily, but the increased activity rapidly fell. O_2 added along with MeOH stabilized the rate of decomposition, the O_2 reacting with the CO to form CO_2.

1104. Frolich, P. K., Fenske, M. R., and Quiggle, D. Studies of Copper Catalysts Prepared From Precipitated Hydroxides. I. Activity as a Function of the Temperature of Precipitation. Jour. Am. Chem. Soc., vol. 51, 1929, pp. 61–65; Chem. Abs., vol. 23, 1929, p. 1342.

Activity for the decomposition of CH_3OH of Cu catalysts prepared from the NH_3 precipitated hydrates varied markedly with the temperature of precipitation. A maximum in activity was observed with catalysts precipitated at about 22°. X-ray examination of the dried gels before reduction indicated that the activity was associated with small particle size. The maximum of the activity curve may have been the result of 2 opposing factors: (1) the tendency for the initial particle size to decrease with decreasing temperature of precipitation; and (2) the tendency for the initially formed particles to grow while drying at 110°.

1105. Frolich, P. K., Fenske, M. R., Perry, L. R., and Hurd, N. L. Studies of Copper Catalysts Prepared From Precipitated Hydroxides. II. Comparison of Sodium Hydroxide and Ammonia as Precipitating Agent. Jour. Am. Chem. Soc., vol. 51, 1929, pp. 187–193; Chem. Abs., vol. 23, 1929, p. 1342.

Cu catalysts prepared by precipitation with NaOH are more active in the decomposition of CH_3OH than those precipitated with NH_3. The difference is due to promoter action of the occluded Na salts. The NaOH-precipitated catalysts, like other promoted Cu catalysts, favor $HCOOCH_3$ rather than HCOOH production from CH_3OH.

Frolich, P. K., Fenske, M. R., Taylor, P. S., and Southwick, C. A. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. II. Synthesis of Methanol With Catalysts Composed of Copper and Zinc. *See* abs. 1099.

1106. Frost, A. V. [Thermodynamics of the Synthesis of Methanol From Water Gas.] Jour. Gen. Chem. (U. S. S. R.), vol. 1, 1931, pp. 367–376; Chem. Abs., vol. 26, 1932, p. 3987.

Free energy of the reaction $CO + 2H_2 \rightleftharpoons MeOH$ is $-\Delta F/4.573T = \log K(RT)^2 = 3925/T - 9.840 \log T + 0.00347T + 14.8$. The value calculated on the basis of Nernst's heat theorem differs from the experimental value by +1.04=0.4, while for other reactions the discrepancy is, according to Eucken and Fried's figures, +0.9.

———. *See* abs. 1584, 2169.

1107. Frost, A. V., Ivannikov, P. Y., Shapiro, M. I., and Zolotov, M. N. [Structure and Genesis of Methanol Catalysts.] Acta physicochim. U. R. S. S., vol. 1, 1934, pp. 511–520; Chem. Abs., vol. 29, 1935, p. 6711.

With various Zn–Cu catalysts under the experimental conditions of Frolich and others (abs. 1100), the composition of the reaction products changed at 369° as observed by them. At 305° and 337° the composition of the products was quite different. The activity of the catalysts decreased only very slowly. Lattice dimensions did not change with the composition of the catalyst, $c = 5.198 \pm 0.004$ A. and $c/a = 1.602 \pm 0.002$. Microscopic and x-ray determination of various preparations of ZnO showed that the crystal size changed from 0.8×10^{-4} to 4.5×10^{-4} cm. on changing the 3-hr. annealing temperature from 110° to 1,300°, and that the adsorptive capacity toward methylene blue was approximately inversely proportional to the crystal size, while the catalytic activity fell still more rapidly. A study of $ZnO \cdot Cr_2O_3$ catalysts in the ratios 3.2 : 1 and 1 : 1 obtained, respectively, by joint precipitation and by simple mixing, showed that the size of the crystal of the 1st was always about ¼ that of pure ZnO crystals, while the latter always gave the same size, 0.9 μ, as for pure Cr_2O_3 on annealing at any temperature above 110°. X-ray analysis showed spinel formation. The catalytic activity decreased rapidly as the annealing temperature was raised with ZnO, 3.2 $ZnO \cdot CrO_3$ and $ZnO \cdot Cr_2O_3$ but was constant for pure Cr_2O_3, except above 900°. For a given treatment 3.2 $ZnO \cdot Cr_2O_3$ was always more active catalytically, as measured by MeOH decomposition, than pure ZnO. The greatest difference was obtained about 100° below the temperature of rapid spinel formation and was attributed to the production of distortions or "Lockerstellen" later stabilized into the crystal.

1108. Fry, A. [Steels for Oil-Cracking Tubes and Hydrogenation Vessels.] Oel u. Kohle, vol. 1, 1933, pp. 184–188; British Chem. Abs., 1934, B, p. 763.

In the production of steels for hydrogenating vessels, methods are used, that is, addition of 6% of Cr or V, followed preferably by special annealing, which bind the C so that it resists reduction by the H_2 under the operating conditions; the further addition of Mo to the steel improves its durability.

1109. Frydlender, J. H. [Manufacture of Synthetic Methanol From Methane.] Rev. prod. chim., vol. 28, 1925, pp. 433–440, 469–476; Chem. Abs., vol. 19, 1925, p. 2928.

Review.

Frye, C. G. *See* abs. 3642a.

1110. Fuchs, W., and Daur, R. [Synthesis of Higher Hydrocarbons From Methane and Carbon Monoxide.] Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 327–329; Chem. Zentralb., 1934, II, p. 1062; Chem. Abs., vol. 29, 1935, p. 6566.

A 2 : 1 mixture of CH_4 and CO at 1 atm. when passed over glowing pumice yields some propylene. Experiments at 500°–550° under a pressure of 240 atm. yielded propylene and also liquid hydrocarbons, but the yield was slight.

1111. Fuchs, W. M. When the Oil Wells Run Dry. Ind. Research Service, Dover, N. H., 1946, 447 pp.; Man-Made Petroleum, chap. VI, pp. 324–392.

Integrated picture of the subject of oil, written for the average citizen in an easily readable and generally understandable manner. Gives a short account of the Bergius and Fischer-Tropsch processes, and the entrance of the United States Government into synthetic fuel production.

1112. Fuel. Catalysts for the Fischer-Tropsch Synthesis. Vol. 25, 1946, p. 123.

Brief notes from CIOS Reports XXV–1, PB 284; XXV–27, PB 289, 890; XXVII–69, PB 415. (*See* abs. 1302, 701, 1327.)

1113. ———. Synthetic Liquid Fuels in the United States. Vol. 25, 1946, pp. 134–137.

Comprehensive summary of the Report of the United States Secretary of the Interior on the Synthetic Liquid Fuels Act covering 1945. A progress report covers investigations already made in coal hydrogenation, liquid fuels from water gas by the Fischer-Tropsch synthesis, synthesis-gas production, oil-shale research, and the production of fuels from agricultural residues.

1114. Fuel Economist. Hydrocarbons From Water Gas. Vol. 9, 1934, p. 303.

It is stated that a plant of semicommercial dimensions is to be erected at Sterkrade-Holten in the Ruhr district at a cost of several million marks, for producing liquid hydrocarbons by the Fischer-Tropsch process. It is expected that erection of the plant will be financed by the Ruhrchemie A.-G., which has already carried out some preliminary work on the process. The plant will have a capacity for producing about 1,000 tons of synthetic motor fuel/yr., as well as lubricating oils and rich hydrocarbon gases which it is proposed to utilize as motor fuel in compressed form in cylinders. The process is based entirely on coal, for the gas used as raw material will be generated from coke. It is suggested that this process will successfully compete with that of the I. G. Farbenindustrie A.-G., whose production costs are said to be about 20 pf./l. of motor fuel produced.

1115. ———. Synthetic Lubricating Oil. Vol. 12, 1936, pp. 113–114.

Summary of status of the research work being conducted at the Fuel Research Station, England. The production of hydrocarbons from water gas by the Fischer synthesis is mentioned.

1116. Fujimoto, H. Catalytic Action of Reduced Nickel on the Methane-Water Reaction. Jour. Soc. Chem. Ind., Japan, vol. 36, Suppl., 1933, pp. 147–148; Chem. Abs., vol. 27, 1933, p. 3661.

Study of the reactions $CH_4 + H_2O = CO + 3H_2$; $CH_4 + 2H_2O = CO_2 + 4H_2$ (1) and $CH_4 = C + 2H_2$ (2) at temperatures 400°–1,000° in the presence of reduced Ni reveals that (1) and (2) begin at about 400° and 700°, respectively, with the reaction velocity of (2) increasing with temperature, while that of (1) passes a maximum at 600° and a minimum at 800°, probably because of the effect of CO on the catalyst. Reaction (2) is accelerated at lower temperatures by adding 10% Al to the catalyst, and reaction (1) is not accelerated but the maximum and minimum are avoided. With 6 times as much H_2O as CH_4, the CO_2 : CO ratio is 2 : 1, while with 2.5 times as much H_2O it is 8 : 1 (700°), and the life of the catalyst is prolonged (250 hr. at 700°).

Fujimura, K. Catalytic Reduction of Carbon Monoxide at Ordinary Pressure. VIII. Iron–Copper Catalyst. *See* abs. 1846.

———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. IX. Additional Tests With a Co–Cu–MgO Catalyst. *See* abs. 1847.

———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. X. Influence of Certain Materials on the Catalytic Action of Cobalt-Copper-Magnesium Oxide Catalysts. *See* abs. 1848.

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressures. XI. *See* abs. 1849.

———. *See* abs. 1845.

Fujimura, K., and Tsuneoka, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressures. XII. *See* abs. 1850.

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressures. XIII, XIV. Nickel Catalysts. *See* abs. 1851.

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressures. XV, XVI. Nickel catalysts. *See* abs. 1852.

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen Under Ordinary Pressure. XVII. General Properties and Chemical Composition of the Reaction Products. *See* abs. 1853.

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen Under Ordinary Pressure. XIX. Composition of the Initial Gas Mixture (1). *See* abs. 1855.

———. Benzine Synthesis From Carbon Monoxide and Hydrogen Under Ordinary Pressure. XX. Composition of the Initial Gas Mixture (2). *See* abs. 1856.

Fujimura, K., Tsuneoka, S., and Kawamichi, K. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XVIII. Effect of Sulfur Compounds on the Nickel Catalyzers. *See* abs. 1854.

Fujisaki, T. *See* abs. 3177, 3178.

Fujita, H. *See* abs. 1913.

Fujita, K. *See* abs. 1892, 1915, 1916, 1917, 1918, 1919, 1920, 1921, 1922, 1923, 1924, 1925, 1926.

Fujita, T. *See* abs. 1908.

Fukushima, I. *See* abs. 1927, 1928, 1929.

Fukushima, R. *See* abs. 1118, 1119, 1120.

Funabashi, W. *See* abs. 1930.

1117. Funasaka, W. [Removal of Sulfur From Gases to Be Used for Synthetic Gasoline.] Chem. Rev., Japan, vol. 3, 1937, pp. 368–386; Chem. Abs., vol. 32, 1938, p. 9464.

Review with 86 refs.

———. Benzine Synthesis From Carbon Monoxide and Hydrogen. L. Removal of Organic Sulful Compounds From Water Gas. *See* abs. 1886.

———. Benzine Synthesis From Carbon Monoxide and Hydrogen. LI. Highly Active Sulfur-Fixation Agent Which Purifies Water Gas to the Highest Degree of Comparatively Low Temperatures Such as 200°–250°. *See* abs. 1887.

———. *See* abs. 1878, 1879, 3466, 3467, 3468.

1118. Funasaka, W., and Fukushima, R. Removal of Organic Sulfur Compounds From Gas Mixtures for Synthesis. X. Influence of Impurities on the Purification of Industrial Gases. Jour. Soc. Chem. Ind. (Japan), vol. 50, 1947, pp. 122–124; Chem. Abs., vol. 44, 1950, p. 9136.

Studies were made on the influence of various gases on the removal of organic S compounds from industrial gases. C_2H_4 had a deleterious effect on Fe and Al catalysts but not on Ni and Cu at 250°. At 400° no effect was detectable. C_6H_6 had no effect, while C_2H_2 had a deleterious effect. Acidic gases, such as CO_2 or HCN, transformed CS_2 to H_2S, especially at high temperature. A high CO_2 content had a deleterious effect at high temperatures. HCN also had a deleterious effect. Air, N_2, and water vapor gave good results. Superimposed effects of various impurities were complicated.

1119. Funasaka, W., Fukushima, R., Jinta, T., Matsubara, I., and Yuguchi, M. Removal of Organic Sulfur Compounds From Gas Mixtures for Synthesis. XI. Removal of Carbon Disulfide and Thiophene From Water Gas and Natural Gas. Jour. Soc. Chem. Ind. (Japan), vol. 50, 1947, pp. 124–125; Chem. Abs., vol. 44, 1950, p. 9136.

CS_2 could be removed by Ni, Cu, and Sn catalysts and thiophene by Fe, Ni, Cu, Mn, Cr, Al, and Mg. With Cr as a catalyst, H_2 was formed.

1120. Funasaka, W., Fukushima, R., Jinta, T., Inaba, T., Matsubara, I., and Yuguchi, M. Removal of Organic Sulfur Compounds From Gas Mixtures for Synthesis. XII. Removal of Ethyl Mercaptan and Ethyl Sulfide From Hydrogen, Natural Gas and Cracking Gas. Jour. Soc. Chem. Ind. (Japan), vol. 50, 1947, pp. 125–126; Chem. Abs., vol. 44, 1950, p. 9136.

EtSH could be removed easily, Et_2S with difficulty. Fe, Ni, Cu, Mn, Cr, Al, and Mg catalysts were suitable for EtSH and Cu and Ni for Et_2S. Et_2S gave H_2S with Cr and Al catalysts.

Funasaka, W., and Katayama, I. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLIV. Purification of the Gaseous Raw Material Used for Benzine Synthesis. 3. Removal of Organic Sulfur by Means of Luxmasse and Admixtures. *See* abs. 1880.

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLV. Purification of the Gaseous Raw Material Used for Benzine Synthesis. 4. Removal of Organic Sulfur by Means of Synthetic Agents. *See* abs. 1881.

Funasaka, W., and Tojo, T. Synthesis of Gasoline From Carbon Monoxide and Hydrogen. LXVII. Desulfurizing Ability of Various Metal Hydroxides. *See* abs. 1903.

Funasaka, W., Fukushima, R., Jinta, T., Matsubara, I., and Yuguchi, M. Removal of Organic Sulfur Compounds From Gas Mixtures for Synthesis. XI. Removal of Carbon Disulfide and Thiophene From Water Gas and Natural Gas. *See* abs. 1119.

Funasaka, W., Fukushima, R., Jinta, T., Inaba, T., Matsubara, I., and Yuguchi, H. Removal of Organic Sulfur Compounds From Gas Mixtures for Synthesis. XII. Removal of Ethyl Mercaptan and Ethyl Sulfide From Hydrogen, Natural Gas, and Cracking Gas. *See* abs. 1120.

1121. Furnas, C. C., and Brown, G. G. Equilibria in the Reduction of Ferric Oxide. Ind. Eng. Chem., vol. 20, 1928, pp. 507–510; Chem. Abs., vol. 22, 1928, p. 2099.

New thermal data on Fe_2O_3 have been used with other data in the literature to compute, by means of the 3d law of thermodynamics the equilibrium constants of 7 reactions involved in the reduction of Fe_2O_3 by CO, C and H_2, and one for the decomposition of Fe_2O_3 into Fe_3O_4 and O_2. Such values of *K* (equilibrium constant) are given for 100°, 250°, 500°, and 750° based upon actual measurable data, and for 1,000° and 1,500° upon extrapolation data. It is shown that (*a*) reduction of Fe_2O_3 by CO and Fe_2O_3 to Fe_3O_4 by H_2 takes place readily at lower temperatures; (*b*) reduction of Fe_2O_3 by C will not occur to any great extent at low temperatures, but the possibility of such reduction with higher temperatures becomes increasingly greater, a conclusion in harmony with experimental evidence but contrary to popular belief (if the gaseous phase is absent no reduction occurs except at high temperatures); (*c*) reduction of Fe_2O_3 by H_2 shows that the power of superheated steam to oxidize metallic Fe decreases with temperature, while its ability to oxidize Fe_3O_4 increases with the temperature; (*d*) data for the decomposition of Fe_2O_3 to Fe_3O_4 and O_2 are not conclusive, but in general the *K* are lower for 1,000° and 1,500° than the experimental work justifies. Inconsistencies are ascribed to the variations in solid phases used. The existence of solid solutions rather than intermediate compounds in the series FeO, Fe_3O_4, Fe_2O_3 may be assumed. Graphs and tables give much condensed information on the matter treated above.

1122. Furness, R. Synthetic Motor Fuels. Ind. Chemist, vol. 1, 1925, pp. 475–480; Chem. Abs., vol. 20, 1926, p. 653.

From the point of view of cost of production in competition with gasoline as motor fuel, the author discusses at some length the following processes: (1) Alcohol by fermentation, (2) synthetic CH_3OH, (3) CH_3OH from CH_4, (4) synthol, (5) synthetic C_6H_6, (6) synthetic C_2H_5OH from C_2H_4, (7) the same from carbide. Much information regarding conditions, yields, and costs for each of the above is given. Gasoline will continue to dominate the liquid-motor-fuel market for such time as its present price is maintained. Synthetic CH_3OH and liquid fuels produced by some simple, catalytic gas reactions are its most likely competitors. Fermentation alcohol, synthetic C_2H_5OH (either from C_2H_2 or C_2H_4), and synthetic C_6H_6 cannot hope to compete with gasoline.

1123. ———. Oils, Fats, and Soaps Industries in 1938. Ind. Chemist, vol. 15, 1939, pp. 37–39, 83–84.

Refers to the German work on the production of fatty acids from hydrocarbons by the Fischer-Tropsch method and their subsequent oxidation to soaps and fats. These processes have little practical significance to the British manufacturer. They are too costly and too complicated to be commercially attractive.

1124. Furth, A. and Munderloh, H. Braunkohle und ihre Chemische Verwendung. Theodor Steinkopff, Dresden; Iron and Coal Trades Rev., vol. 163, Aug. 10, 1951, p. 310.

Statistical data and a summary of the theories concerning the origin of brown coal and the structure of the derivatives are first presented followed by a description of low-temperature carbonization of brown coal. The most significant recent development is the introduction of the Lurgi furnace with forced gas circulation and electrostatic tar precipitation. All pertinent patent specifications are reviewed. Gas scrubbing methods for the production of light fractions of oils are presented together with methods for the utilization of brown coal coke. Gas producers are unable to utilize raw brown coal, the moisture content of which is 50–55%, but several types of producers fed with brown-coal briquets are included. Distillation of the tar for production of benzol, diesel fuel, lubricating oil, fuel oil, paraffin wax and pitch, and the solvent extraction and cracking of tar are described. The various processes for the production of synthetic fuel, including the Fischer-Tropsch hydrogenation process, as applied to brown coal are considered. A summary of the patent literature and a description of the drying and briquetting processes complete the book.

1125. Fussteig, R. [Gasoline From Coal.] Mat. grasses, vol. 25, 1933, pp. 9810–9811; Chem. Zentralb., 1933, II, p. 1951.

Review of development of coal liquefaction, Bergius process, Fischer-Tropsch process, and hydrogenation according to Sabatier, with special reference to the problem of catalysts.

1126. ———. [New Methods for the Production of Automobile Gasoline With Coal as the Raw Material.] Mat. grasses, vol. 25, 1933, pp. 9863–9868; Chem. Zentralb., 1934, I, p. 980.

Discusses Bergius process and conversion of water gas.

1127. ———. Synthesis of Lubricating Oil by Polymerization of Gaseous Hydrocarbons. Petrol. Eng., vol. 9, Feb. 1938, pp. 120, 123, 124, 127.

1128. ———. Synthesis of Petroleumlike Hydrocarbons From Carbonaceous Material. Petrol. Eng., vol. 11, No. 8, 1940, pp. 95–96, 98, 100; Chem. Abs., vol. 34, 1940, p. 7086.

Discusses fundamental principles of the Fischer synthesis and the allied processes with emphasis on the production of the starting material, water gas. The efficiency of the Fischer synthesis centers upon the control of reaction conditions, especially the ratio of $CO:H_2$, pressure, and temperature. Mentions effects of changes in reaction conditions, especially on quality of product. A flowsheet is given of the Fischer process combined with true vapor-phase cracking, and typical yields are tabulated. The necessity for the desulfurization of the starting gases is stressed, the maximum permissible S content being given as 2 mg. per $m.^3$ Catalytic desulfurization with alkali-activated Fe oxide is briefly outlined. Paraffin wax can also be synthesized by the Fischer process. A 2-stage synthesis in which the catalyst temperature is kept 5°–10° higher in the 2d stage than in the 1st is claimed to increase the yield of hydrocarbons from 110 to 125–130 gm. per $m.^3$ gases.

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1129. Gall, D. Production of Lubricating Oils From the Olefins Produced in the Fischer-Tropsch Synthesis. Jour. Soc. Chem. Ind., vol. 65, 1946, pp. 185–189; Chem. Abs., vol. 40, 1946, p. 7582.

Preparation of lubricating oils by polymerization with $AlCl_3$ of the olefins present in the primary product obtained by synthesis from CO and H_2 (1:2) over a Co catalyst at atmospheric pressure has been carried out in 2-gal. batches. The effect of varying the temperature, catalyst, and boiling range of the starting material on the reaction and its products is described. Two fractions b. 40°–140° and 140°–210°, with 8.6 and 28% by weight, respectively, of olefins were polymerized at the reflux point to a material apparently above the original boiling range. The yield of lubricating oil of similar viscosity is much lower from the higher-boiling fraction; this is due partly to the relatively higher proportion of olefins which are lost as $AlCl_3$ complex and partly to a tendency of the olefins of higher molecular weight to give oils of lower viscosity, so that these have to be topped to a higher initial boiling point to give the same viscosity as the polymers from the lower olefins. The use of higher olefins gives a lubricating-oil fraction of higher viscosity index, but there appears to be little difference in the other properties tested. Investigations on the effect of varying the reaction temperature and the proportion of catalyst with the 40°–140° fraction were made. It was found that increasing the proportion of catalyst increases the reaction velocity and the viscosity of the product but lowers the yield, whereas increasing the temperature increases the rate of reaction but decreases both the yield and the viscosity of the lubricating-oil fraction but has little effect on the viscosity index. The oils obtained possess properties which approximate the requirements of Air Ministry Spec. D. T. D. 109 for aircraft lubricants in all respects except the increase in viscosity on oxidation. It was found possible to overcome this disability by subjecting the oils to a carefully controlled hydrogenation in the presence of MoS_2 at 200° and 200 atm. H_2 pressure, using 20% by weight of catalyst calculated on the oil charged.

1130. ———. Characteristics of Fischer-Tropsch Waxes. Inst. Petrol. Rev., vol. 1, Oct. 1947, pp. 336–337.

The mixture of aliphatic hydrocarbons produced by the Fischer-Tropsch process ranges from CH_4 to solid waxes. The boiling range of the individual products varies with the reaction conditions and the catalyst. Wax production is favored by increase in pressure and by catalysts in the order of Co, Fe, Ru. The Ruhrchemie prepared soft, block, and hard waxes from the medium-pressure synthesis product, the fraction boiling above 320° being divided by distillation in vacuo into a residue boiling above 460° at 760 mm., which constituted the hard wax, and two distillates, from which the soft and block waxes were obtained by sweating. Similar low-melting waxes can be prepared from the atmospheric pressure product. No data are available for comparison of the Fischer-Tropsch waxes with natural hydrocarbon waxes in respect of properties such as solvent retentivity, tensile strength, solubility, viscosity, etc. It is known, however, that the soft and block waxes are closely similar to the corresponding petroleum paraffin waxes. The value of the high-melting waxes is not so readily assessed, and from what is known of their structure it is doubtful if they are adequate substitutes for natural waxes of high-melting point and hardness.

———. *See* abs. 671, 675, 1334, 1335, 1335a, 1336.

1131. Gall, D., and Hall, C. C. Production of Fatty Acids by the Oxidation of Fischer-Tropsch Waxes. Fuel, vol. 27, No. 5, 1948, pp. 155–167.

A study has been made of the effects of temperature, time, rate and distribution of air stream, nature and amount of catalyst, composition of raw material, and recirculation of nonacidic products, on the reaction rate and the yield and properties of the fatty acids obtained by the liquid-phase oxidation of the high-boiling fractions of Fischer-Tropsch primary products. The rate of air flow has a comparatively small effect on the reaction velocity although an optimum rate can be found. It is desirable to distribute the air stream over the whole cross-sectional area of the reaction tube, but increase in the fineness of subdivision over that afforded by coarse, sintered glass has no favorable effect. The velocity of oxidation increases with increase in the reaction temperature over the range 100°–140°, but at the lower temperatures acids of higher quality are obtained. Optimum results were obtained by oxidizing a mixture of approximately equal proportions of the saturated fraction of boiling range 300°–375° and unsaponifiable material from a previous oxidation to a final saponification number of 150, by passing 16.5 l of air per 100 gm. raw material at 110°, in the presence of an oil-soluble Mn catalyst. Compounds of Mn are preferable to those of Co, giving a higher reaction velocity and products of good quality. The efficiency of the catalyst depends upon its solubility in the reaction mixture. By returning the unsaponifiable material formed to a subsequent oxidation, it is possible to obtain over 90% conversion of wax to fatty acids, with the advantages of a higher reaction velocity and a better quality C_{10}–C_{20} acids than are obtained when wax is oxidized alone. Using this technique a 50–70% conversion is possible. The maximum space-time output of these acids is obtained by oxidizing a mixture of approximately equal proportions of wax and recovered unsaponifiable material. The acids in the range C_{10}–C_{20} give good soaps, which, however, are unsuitable for toilet purposes because of the unpleasant odor left on the skin.

1131a. Gall, D., Gibson, E. J., and Hall, C. C. Distribution of Alcohols in the Products of the Fischer-Tropsch Synthesis. Proc. Pure Applied Chem., 12th Internat. Cong., Sept. 1951; Jour. Appl. Chem. (U. S. S. R.), vol. 2, 1952, pp. 371–380.

Alcohol-rich product obtained by Fischer-Tropsch synthesis at 160°–175° and 150 p. s. i. g. in the presence of a Co catalyst has been examined. It was found that *n*-primary alcohols constituted 40 wt. % of the organic liquid products and 92.4% of the total oxygenated products. The proportions of acids and carbonyl compounds were, therefore, markedly lower than those reported to be present in an Fe-catalyst product of the hydrocol type. The proportion of MeOH present was very low, EtOH was present in the largest proportion and the proportions of alcohols higher than PrOH decreased with increasing C number. The proportion of PrOH was less than that of BuOH or AmOH so that the C-number distribution curve for the alcohols showed a marked inflexion in the C_3–C_4 region, which is not shown by the published distribution curve for the alcohols in the hydrocol product. From a study of the relative rates of decomposition of a series of *n*-primary alcohols at 150° in the presence of H_2 and a Co catalyst, it was possible to plot a curve relating alcohol stability and C number. This curve resembled the distribution curve in showing a low value for C_1, a maximum at C_2 and a marked inflexion in the C_3–C_4 region, suggesting that the individual alcohols are present in the synthesis products in proportions which are determined, at least in part, by their relative stabilities under the synthesis conditions. It is considered that the alcohol distribution curve is of a form which would be predicted if the mechanism of alcohol formation involved stepwise addition of methylene radicals to 1 end of a growing chain terminated by a hydroxymethylene radical, and if the survival of the alcohols was controlled by their relative stabilities. It is concluded that there is a balance of evidence in favor of the view that alcohols are the precursors of hydrocarbons in the synthesis.

1132. Galle, E. [Motor Fuel From Czechoslovak Coal.] Montan. Rundschau, vol. 29, No. 6, 1937, pp. 1–7; Petrol. Ztschr. vol. 33, No. 10, 1937, p. 4; Chem. Zentralb., I, 1937, p. 3902.

Reviews the various processes for the production of motor fuels and the possibilities of their use in Czechoslovakia. Economically, the facts appear to favor the Bergius process over the Fischer process.

1133. ———. [Chemical Possibilities for the Production of Motor Fuels.] Montan. Rundschau, vol. 30, 1938, No. 15, pp. 1–8; No. 16, pp. 1–4; Chem. Abs., vol. 32, 1938, p. 8739.

After a description of production of oil and gasoline from coal by the Fischer process, the Bergius hydrogenation process and the synthesis of MeOH from coke, details are given of high-pressure hydrogenation and of the Fischer-Tropsch gasoline synthesis. Gasoline obtained by high-pressure hydrogenation has octane numbers of 70–75, and by special treatment octane values of 80–90 can be obtained. The Fischer-Tropsch process yields gasolines with 45–50 octane values, and by special treatment this can be raised to 60–62.

1134. ———. [Production of Liquid Fuels by Chemical Methods.] Petrol. Ztschr., vol. 34, No. 19, 1938, pp. 1–12.

Reviews development of the coal-hydrogenation and Fischer-Tropsch processes.

Gallissot, M. *See* abs. 2273.

1135. Gallo, G. and Correlli, R. [Synthetic Production of Liquid Fuels.] Atti cong. nazl. chim. pura applicata, 1923, p. 257; Chem. Abs., vol. 18, 1924, p. 2594.

Preliminary work is described on the cracking of vegetable oils by a method similar to that used by Mailhe for obtaining petroleum products from such oils. The vegetable oil is decomposed by superheated steam in the presence of an alkaline earth, the products are led in the vapor state over pumice stone containing FeO at 550°–560° and the new products passed over pumice stone containing Ni at 200°–250° where hydrogenation is carried out. The FeO remains unaltered on account of the oxidizing action of the H_2O and simultaneous reducing action of the oil vapor. A gaseous product of the following percentage composition was obtained: CO_2 4.2, heavy hydrocarbons 33.5, CO 3.7, saturated hydrocarbons 43.4, H_2 15.2. A yellowish brown, slightly fluorescent, mobile liquid was also recovered with a yield of 60.65% of the original oil, an aromatic odor, 0.5% acidity, calculated as oleic acid, saponifiable 0.46%, giving in large part nitro derivatives with HNO_3–H_2SO_4 mixture and yielding in percentage on fractional distillation: 45°–200°, 24.5; 200°–300°, 41; 300°–350°, 29.5; tar residue 5%.

Galloway, A. E. *See* abs. 373, 374, 375.

1136. Galt, J. K., Matthias, B. T., and Remeika, J. P. Properties of Single Crystals of Nickel Ferrite. Physiol. Rev., vol. 79, 1950, pp. 391–392; Chem. Abs., vol. 44, 1950, p. 8712.

Mixture of 16–17 gm. borax glass, 6.4 gm. Fe_2O_3, and 3.0 gm. NiO was heated in Pt to 1,330°, held there 10–12 hr., and cooled $\approx$ 2°/hr. for 25–40 hr.; the furnace was then turned off completely. Crystals of $NiFe_2O_4$ up to 2 mm. on a side, with impurities $<0.5\%$, were obtained. The dielectric constant, the saturation magnetization, the magnetic anisotropy constant K_1, and the complex initial permeability were measured.

1137. Gandini, A. [Analytical Examination of Two New Methods for the Reduction of Iron Ores by Carbon Monoxide and Their Relation to the Iron-Ore and Fuel Resources of Italy.] Atti cong. nazl. chim. ind., 1924, pp. 311–329; Chem. Abs., vol. 19, 1925, p. 1394.

Most promising methods for the reduction of Fe ore are those involving the production of CO and direct reduction by the latter, particularly that of Bourcoud and the newly developed process of Gandini. The Bourcoud process is described in detail, with a general discussion of the physical chemistry involved in the reduction of Fe oxides by CO. The velocity of this reduction and the yield of Fe at a given temperature are shown to be functions of the pressure and concentration of the CO, of the square root of its kinetic energy at the moment of impact with the oxides, of the absolute number of CO molecules, and of the degree of subdivision of the Fe ore.

1138. Ganswindt, A. [Commercial Benzines.] Neueste Erfin. u. Erfahr., vol. 37, 1920, pp. 74–79; Chim. et ind., vol. 5, 1921, p. 416; Chem. Abs., vol. 15, 1921, p. 3203.

Brief review of the different grades of benzine, their origin, and methods of preparation, including the catalytic reaction of H_2 on CO or on CO_2 in the presence of Co oxide or of osmic acid.

1139. Ganz, S. N. [Obtaining Synthetic Methanol From Waste Gases.] Jour. Chem. Ind. (U. S. S. R.), vol. 17, No. 9, 1940, pp. 45–46; Chem. Abs., vol. 35, 1941, p. 1758.

Discusses apparatus.

1140. Garcia y Lastres, N. [Manufacture of Synthetic Petroleum Products.] Cuerpo de Ingenieros de Minas, Bull. 126, Peru, 1940, 347 pp.

Review of production of fuels in Germany, Scotland, and England by various treatments of coal, lignite, tars, and oil shale. Discusses carbonization, hydrogenation, distillation, and synthesis.

Garcin, M. *See* abs. 2329.

Gardner, J. B. *See* abs. 295, 2444.

1141. Garfinkel, I. M. [Carbon Monoxide the Main Factor in Crude-Oil Synthesis.] Neftyanoe Khoz., vol. 15, 1928, pp. 556–558; Chem. Abs., vol. 23, 1929, p. 4807.

Reviews various synthetic crude-oil processes.

1142. Garner, F. H. Liquid Fuels and Other Products From Petroleum and Coal. Internat. Cong. Pure Appl. Chem., 11th Cong., London, July 1947; Jour. Inst. Petrol., vol. 33, 1947, pp. 678–686; Fuel Abs., vol. 2, No. 2, August 1947, p. 61.

Development of hydrogenation and Fischer-Tropsch processes has made all natural sources of hydrocarbons—natural gas, petroleum, coal, shale—available for the production of liquid fuels, of all types of hydrocarbons, C_2H_2, olefins, paraffins and aromatics, and of synthetic chemicals. Application of the Fischer-Tropsch process may lead, as in the case of petroleum, to production of synthetic chemicals. The most important products, such as plastics, synthetic fibers and detergents, made from synthetic chemicals, are being derived to an increasing extent from hydrocarbon sources.

1143. ———. Extractive Distillation. Ind. Chemist, vol. 25, 1949, pp. 238–242.

Discusses process in detail. It may be used in separating alcohols, aldehydes, ketones, and acid present in Fischer-Tropsch products. Gives list of 15 refs.

1144. Garner, W. E., and Kingman, F. E. T. Adsorption of Hydrogen and Carbon Monoxide on Oxide Catalysts. Nature, vol. 126, 1930, p. 352; Chem. Abs., vol. 24, 1930, p. 5567.

H_2 or CO adsorbed at room temperature on ZnO–Cr_2O_3 catalysts was given off at 100°–120° but after 20–30 min. was readsorbed on the surface of the catalysts. On raising the temperature further, no gas was given off up to 350°, when H_2O or CO_2 was liberated. Physically adsorbed gas must leave the surface before it can chemically combine with metallic oxides.

1145. ———. Heat of Adsorption of Hydrogen and Carbon Monoxide on Zinc and Chromium Oxide Catalysts. Trans. Faraday Soc. vol. 27, 1931, pp. 322–333; Chem. Abs. vol. 25, 1931, p. 4758.

Heats of adsorption and adsorptive capacity of H_2 and CO on ZnO, Cr_2O_3, and ZnO–Cr_2O_3 catalysts were measured by means of a vacuum calorimeter previously described. The heats of adsorption ranged from 25–10 cal. per gm. mol., the maximum value being obtained for the first small quantities adsorbed. The heat of adsorption of CO on ZnO is the same as that of ZnO–Cr_2O_3, although the adsorptive capacity is much greater in the latter case. This indicates that the greater efficiency of the mixed catalyst is due to an enlargement of the internal area of the catalyst. Cr_2O_3 and ZnO did not adsorb H_2 as strongly as the mixed catalyst, but the Cr_2O_3 adsorbed CO very readily. At low temperatures H_2 and CO are mainly adsorbed without disruption of the molecules, but at 100° and over the adsorption was irreversible, and the gas could only be removed as water and CO_2, respectively, by heating to high temperatures. In the case of the mixed catalyst, the rate of evolution from 1 type of adsorbed film was greater than the rate of condensation to a second type of film, so that on heating to about 100° of a catalyst that had adsorbed H_2 at 20°, there occurred an evolution of H_2 which was followed by slow readsorption.

1146. Garran, R. R. Equilibria at High Temperatures in the System Iron-Oxygen-Carbon. Trans. Faraday Soc. vol. 24, 1928, pp. 201–207; Chem. Abs. vol. 22, 1928, p. 2099.

Most of the experimental results dealing with this system given in the literature were made below 1,000°. Extrapolation to temperatures above 1,000° is very uncertain. Experimental results are given covering the temperature range 600°–1,300°.

GARRISON, W. *See* abs. 2891.

1147. GAS AGE. Gasoline From Natural Gas. Vol. 97, No. 3, 1946, p. 50.

Carthage Hydrocol, Inc., is proposing to build a plant near Brownsville, Texas at a cost of approximately $14,000,000 to manufacture gasoline from natural gas by the Hydrocol process. The plant is being designed for a capacity of processing approximately 60,000,000 cu. ft. of gas per day with a calculated production of 5,900 bbl. of gasoline and 1,100 bbl. of Diesel and other oils. The participators are named. (*See* abs. 2777).

1148. ———. Carthage Hydrocol to Use Hidalgo County Natural Gas. Vol. 98, No. 8, 1946, pp. 44, 46.

Most of the natural gas to be used in gasoline conversion at the Carthage Hydrocol plant will be supplied by fields in Hidalgo County, Texas. Both the La Gloria Corp. and the Gulf States Oil Co., stockholders in the Hydrocol plant, own production in these fields. Hydrocol is now negotiating a contract with the Brownsville Navigation District for construction of the gasoline-conversion plant. An estimated 55 miles of gas line will transport the gas from the fields to the plant.

1149. ———. Synthetic Research. Vol. 98, No. 8, 1946, p. 52.

It is announced by J. A. Glen, Minister of Resources, that Canada is giving serious attention to development of synthetic fuel processes. A sum of $50,000 has been voted for a small-scale pilot plant in Ottawa to experiment with synthetic liquid fuel. An official has been sent to Germany to investigate plants, and research will extend to all forms of hydrogenation. A fuel-research board will be set up to direct an overall program of fuel research.

1150. GAS JOURNAL. Indirect Hydrogenation. Vol. 215, 1936, p. 482; Colliery Guard., vol. 153, 1936, p. 419.

Koppers Co. is closely identified with the Fischer-Tropsch process. In 1935, the Koppers Co. of Essen received an order to supply the plant to produce the mixture of CO and H_2 (the "synthesis gas") necessary for this process. This order comprised the whole of the plant to produce in a sufficiently pure condition the gases for the Fischer Tropsch installation at Braunkohle-Benzin A.-G., Ruhland, for the Braunkohle-Benzin A.-G., Berlin. The first section of the plant has a capacity of 900,000 cu. ft. of synthesis gas per hr., which corresponds to a yearly production of 25,000 tons of primary products. The Koppers plant at Braunkohle-Benzin A.-G., was put into operation in April, 1936. Since then Koppers has received a further order for the extension of this installation to produce an additional 4,500,000 cu. ft. of synthesis gas per hr., for the production of which 5 new units will be needed. All the Braunkohle-Benzin A.-G. units manufacture the synthesis gases from brown-coal briquets. At another plant ordered in 1935 by the Rheinpreussen Company, Homberg, identification of the Koppers Co. with the Fischer-Tropsch process has been carried a stage farther. Originally the Koppers Co. had to provide the synthesis gases only, but now the arrangement has been extended so that Firma Heinrich Koppers G.m.b.H., as general contractors, have charge of the designing, and the supervision of the erection and starting of the whole of the plant for the production of liquid power fuels. This plant is to produce 30,000 tons of primary product per year, the raw materials being blast furnace coke and coke oven gas. The products will consist of motor spirit (benzine), diesel oil, soft and hard paraffin wax, and oils for the production of domestic fats, and other chemical uses.

1151. ———. Queensland's Coal Resources. Vol. 261, 1950, p. 103.

As a result of a preliminary survey, it is concluded that Queensland has cheap, abundant supplies of coal of a wide range of types. Many high-class coking coals are available. There is a prima facia case for a thorough investigation of the potentialities in developing an oil-from-coal industry, using one of the modern variants of the Fischer-Tropsch process.

1152. GAS- UND WASSERFACH. [Hydrocarbon Synthesis From Water Gas.] Vol. 77, 1934, p. 798; Fuel Economist, vol. 10, 1935, p. 759.

Ruhrchemie at Oberhausen-Holten is operating the Fischer process in a plant of 1,000-ton per yr. capacity. The process works at atmospheric pressure and at a temperature of 190°–210° C. The gases used for the synthesis are water gas or cracked coke oven gas, both of which are carefully purified, particularly from organic S, in order to prevent the rapid deterioration of the catalyst (Ni-Al-Mn precipitated on kieselguhr). The hydrocarbons formed range from petrol to solid paraffin wax, the respective quantity being about ⅔ of petrol and ⅓ of fuel and heavy oils. No detailed information is as yet available with regard to the yield obtained on the large-scale plant and the cost of operation. If the process should prove economical, the Ruhrchemie will erect an installation of some magnitude. Likewise, the Colliery Victor at Rauxel contemplates erection of a plant with an annual capacity of 25,000 tons of petrol. The primary object of this plant is to find an outlet for the gas (presumably H_2) not required in the synthetic NH_3 works attached to the colliery. The synthetic NH_3 works at Scholven, belonging to the Prussian State Colliery, Rocklinghausen, has the same object in view but intends to employ the hydrogenation process of the I. G. Farbenindustrie, if the experiments with hydrogenation of coal now carried out at Oppau yield satisfactory results.

1153. GAS WORLD. Synthetic Methyl Alcohol. Vol. 82, 1925, p. 416.

Synthetic production of MeOH is now successful on a commercial scale. In 1921 Patart and in 1922 the Badische Anilin Co. patented the catalysis of CO and H_2 at high pressures and moderate temperatures in the presence of catalysts. The reactions are:

$$(a)\ CO+2H_2 \rightleftharpoons CH_3OH.$$

$$(b)\ CH_3OH+H_2 \rightleftharpoons CH_4+H_2O.$$

$$(c)\ CH_3OH+CO \rightleftharpoons CH_4+CO_2.$$

Reaction (*a*) is favored by high pressures, since it is accompanied by a diminution in volume. Reactions (*b*) and (*c*) are unaffected by pressure, since there is no change in volume, but since they are endothermic from left to right, they are favored by high temperatures. By keeping the temperature low the production of CH_3OH is favored. With a special saline catalyzer 1 $m.^3$ of CO and 2 of H_2 at 250 atm. and 220°–300° C. will yield 1.36 kg. of CH_3OH of remarkable purity, free from aldehydes and acetone in an apparatus similar to that used for synthesis of NH_3. By raising the temperature higher, alcohols and CH_4 are produced. The economic importance of this reaction is evident.

1154. ———. Liquid Fuels and the Gas Industry. Vol. 83, 1925, pp. 8–9 (Suppl.); Chem. Abs., vol. 20, 1926, p. 980.

Liquid-fuel production should be taken over by the gas industry and not allowed to become a competitor in other hands. Synthetic NH_3 is cited as a commercial undertaking lost to the gas industry. The production of liquid fuels from coal and water gas is discussed.

1155. ———. Petrol Synthesis. Vol. 103, 1935, p. 253.

2 more Fischer plants for the production of motor fuel from water gas have been installed in Germany—1 by the Ruhrchemie A.-G. at Oberhausen-Holten, the other by the Klöckner combine at Castrop-Rauxel. The combined capacity is estimated at 25,000 tons of gasoline per year.

1156. ———. Progress in Coal Processing and Byproduct Treatment. Vol. 105, Coking Sec., Sept. 5, 1936, p. 22.

Discusses recent Koppers activities in constructing the plants at Brabag and Homberg (Rheinpreussen Co.) for producing the synthesis gases for the Fischer-Tropsch process.

1157. ———. Oil and Petrol From Coal. Vol. 120, 1944, pp. 487–489.

An editorial urging greater British development and utilization of the Fischer-Tropsch process for the production of liquid fuels from British coal. The point is emphasized, based on the recent lecture by J. G. King before the Junior Institution of Engineers, that the logical development is toward combining coal carbonization with the Fischer-Tropsch synthesis, whereby only 3.45 tons of coal would be required to produce 1 ton of primary product at a thermal efficiency of 42% instead of the 25% usually quoted.

1158. ———. Reconstructed Ruhrchemie Co. Vol. 127, 1947, p. 174.

Nearly 5,000 workers are now employed in the Ruhrchemie works; only rarely has it employed as many workers in the past. The N_2 plant is working with 3 8-hr. shifts daily, and as soon as permission is granted for the processing of coal–H_2 the works will extend its activities to produce synthetic gasoline and other products such as alcohol, lubricating oil, fatty acids, and detergents.

1159. ———. Gas-Synthesis Demonstration Plant. Vol. 132, 1950, p. 654.

General, brief description of the United States Bureau of Mines synthetic liquid fuels demonstration plant.

1159a. ———. American Gas-Synthesis Experiment. Vol. 135, 1952, pp. 423–424.

Summary of a report of the second integrated plant test at the Bureau of Mines Fischer-Tropsch demonstration plant at Louisiana, Mo., at the end of a 25-day run.

GAUDECHON, H. *See* abs. 250.

1160. GAUGER, A. W. Gasification of Solid and Liquid Fuels. Physical Chemistry and Technology of Fuels. 21st Ann. Priestley Lectures, Pennsylvania State College, State College, Pa., 1947, pp. 65–84; Fuel, vol. 26, No. 5, 1947, pp. 138–144.

Describes gas-making processes that depend upon heat and those which involve reactions of hot C with steam and CO_2, such as water gas, producer gas, oil, and synthesis gas. Discusses the thermodynamic data connected with these reactions and the physical chemistry thereof. Some results of commercial plant tests at Trail, B. C., on an O_2-blown gas producer utilizing anthracite coal are presented. Two new gasification processes of major interest, the Lurgi and the Winkler, are given detailed consideration.

1161. ———. Interconversion of Solid, Liquid, and Gaseous Fuels. Physical Chemistry and Technology of Fuels. 21st Ann. Priestley Lectures, Pennsylvania State College, State College, Pa., 1947, pp. 43–63.

General procedure in the commercial hydrogenation of coal is described. Whereas in Europe it required from 4–4.5 tons of coal to produce 1 ton of gasoline at an overall thermal efficiency of about 42%, the Bureau of Mines has recently demonstrated that 1 ton of gasoline can be produced on an improved plant from 3.14 tons of coal at an overall thermal efficiency of 56.4% compared to 28.9% for a typical German plant. The chemistry of coal hydrogenation and the effect of various factors, such as coal composition, turbulence, liquefaction, H adsorption, catalysts, etc., on the hydrogenation process are briefly reviewed. It has previously been indicated that the primary process in hydrogenation is the formation of heavy oil, which is later converted into lighter products and hydrocarbon gases, but it is recently reported that the primary product is asphalt. As to the character of the products formed, the subject is still exceedingly complex, but current studies of the middle oil are developing considerable interest and probably will lead to products of commercial value. The isolation of several polynuclear aromatic compounds of high molecular weight has already been reported. The synthesis of MeOH and other hydrocarbons from CO and H_2 is discussed at some length and the thermodynamics and the mechanism of the processes set forth in detail. Considers commercial development of the synthetic oil processes and their economic possibilities.

———. *See* abs. 930.

1162. GAUGER, A. W., AND TAYLOR, H. S. Influence of Temperature Pressure and Supporting Material for the Catalyst on the Adsorption of Gases by Nickel. Jour. Am. Chem. Soc., vol. 45, 1923, pp. 920–928; Chem. Abs. vol. 17, 1923, p. 1913.

Isotherms of the absorption of H_2 on Ni, using N_2 as a reference gas, show that there exists a definite saturation capaicity of Ni for H_2 which depends on the temperature. A value of approximately 2,500 cal. per gm. mol. has been deduced from variation of the saturation pressure with temperature for the heat of adsorption of H_2 on Ni, whereas by a different method Rideal obtained a value of 12,000 cal. The use of an inert material for catalyst support increases greatly the adsorptive capacity per gm. of Ni and yields a catalyst capable of standing more severe heat treatment.

1163. GAUGER, A. W., AND WRIGHT, C. C. Coal as Related to the Liquid-Fuel Industry. Min. Cong. Jour., vol. 30, No. 4, 1944, pp. 27–30; Chem. Abs., vol. 38, 1944, p. 3446.

Brief descriptions of the Bergius, Fischer-Tropsch, and Pott-Broche processes.

GAUKHMAN, S. S. *See* abs. 2888, 2889, 2890.

1164. GAUKHMAN, S. S., AND ROITER, V. A. [Role of Sorption of Nitrogen in the Mechanism of Ammonia Synthesis in the Presence of Technical Iron Catalyst.] Jour. Phys. Chem. (U. S. S. R.), vol. 11, 1938, pp. 569–577; Chem. Abs. vol. 33, 1939, p. 4386.

Adsorption of N_2 and H_2 on technical catalyst 340 (composition is not disclosed) was investigated at —184°–425° and —184°–250°, respectively, at a constant pressure of 435 mm. With H_2, a definite sorption process was observed in the region below 250° K. and another up to 500° K. The energy of activation of the low-temperature process increased from 7,200 to 10,680 cal. per mol., with increase of surface from 0.5 to 3.5 $cm.^2$ One type of N_2 sorption was observed. The energy of activation of low-temperature adsorption of N_2 was calculated to be equal to 1,500 cal. per mol. The difference in the catalytic activity of the previously described Fe–Mo cataylst cannot be explained by difference in the magnitude of total surface, since the variation of the latter was inverse to the variation in the catalytic activity. The velocity of sorption process in the presence of this catalyst increased with the increase of the catalytic activity. The velocity of formation of NH_3 at 375° was near that of sorption of N_2 under the same conditions. The energy of activation of the synthesis was considerably lower than that of the sorption of N_2.

1165. ———. [Comparative Characteristics of the Adsorptive and Catalytic Properties of Variously Prepared Synthetic Ammonia Iron Catalysts.] Jour. Phys. Chem. (U. S. S. R.), vol. 13, 1939, pp. 593–599; Chem. Abs. vol. 34, 1940, p. 1543.

Adsorption isotherms for H_2 and N_2 on 2 Fe catalysts promoted by 2% Al_2O_3 are given for temperatures 184°–425°. Physical adsorption was found at 184°, 2 types of activated adsorption at 250°–425° on the sintered catalyst only. For the NH_3 synthesis at 360°–385° the catalytic activity of the sintered catalyst was proportional to the activated adsorption.

1166. GAUTIER, A. [Action of Carbon Monoxide on Steam at Red Heat, and Action of Hydrogen on Carbon Dioxide.] Bull. soc. chim., vol. 35, 1906, pp. 929–934; Compt. rend., vol. 142, 1906, pp. 1382–1387; Jour. Soc. Chem. Ind. (London), vol. 25, 1906, p. 1145; Chem. Abs., vol. 1, 1906, p. 274.

Boudouard (*see* abs. 321) determined the ratio, CO : CO_2, in the equilibrium between CO, steam, CO_2, and H_2 at different temperatures; and Hahn (*see* abs. 1310) determined the coefficient, $K=\frac{CO\times H_2O}{CO_2\times H_2}$, at different temperatures. The author shows that, when a current of CO, mixed with a varying excess of steam, is passed through a porcelain tube heated to 1,200°–1,250° C. at the rate of about 1 liter of the mixed gases per hr., or when a dry mixture of equal volumes of CO_2 and H_2 is similarly treated at 1,300,° the reaction proceeds until the volume of H_2 is about double that of CO. The reactions correspond with the equations: $3CO+3\ H_2O=CO+H_2O+2\ H_2+2CO_2$. $3CO_2+3\ H_2=CO+H_2O+2\ H_2+2\ CO_2$. Under these conditions, any mixture of CO, steam, H_2, and CO_2 tends toward the composition, $CO+H_2O+2H_2+2\ CO_2$ Small quantities of formic acid, but no formaldehyde, are produced. These results are discussed with reference to the composition of volcanic gases, and attention is directed to the occurrence of formic acid in certain hot mineral springs.

1167. ———. [Reactions Between Hydrogen and Carbon Monoxide and the Effect of Steam on Carbon Monoxide at Elevated Temperature.] Compt. rend., vol. 150, 1910, pp. 1564–1568; Bull. soc. chim., vol. 7, 1910, pp. 765–768; Chem. Zentralb., 1910, II, p. 292; Chem. Abs., vol. 6, 1912, p. 287; vol. 4, 1910, pp. 2251, 3048.

Reduction of CO by H_2 begins approximately at 400°, resulting in the formation of H_2O, C, and some CH_4. The mutual reactions are limited and equilibrium is reached at approximately 1,000°. The formation of CH_4 is favored by a higher % CH_4 and by a greater velocity to prevent its splitting off at red heat. Between 450° and 650° traces of formol are formed but disappear again at 950°. On passing a mixture of 1 vol. CO and 6 vol. H_2 at a speed of 1 l. per hr. through a porcelain tube heated to 1,200°, there was obtained, after removal of the CO and CO_2 from the end gas, a mixture of 99.8% H_2 and 0.2% CH_4. At 1,300° and a 3 times greater gas velocity, 98.65% H_2 and 1.35% CH_4 were obtained. The higher velocity thus appears to prevent decomposition of the CH_4 formed.

1168. GAUTIER, A., AND CLAUSMANN, P. [Action of Iron and Its Oxides at Red Heat on Carbon Monoxide.] Compt. rend., vol. 151, 1910, pp. 16–22; Chem. Zentralb., 1910, II, p. 729; Chem. Abs., vol. 5, 1911, p. 53.

Action of CO on Fe yields C, carbides, and CO_2. If the oxides are mixed with Fe, CO_2, free C and several carbides of which the most probable are $Fe_{12}C$ and Fe_3C—the former more easily attacked by H_2SO_4—are formed. The action of acids upon the carbides thus formed gave CH_4, H_2, and a small amount of petroleum compounds. The action of steam at red heat upon the carbides formed as above was studied for its bearing on geological problems. There were formed at 500°–600° and at 800°–900°: H_2, 98.23 and 23.17; CH_4, 1.77 and 3.44; CO, 0.00 and 65.10; and CO_2, 0.00 and 8.33. It is believed that the high pressures within the earth's crust would also produce the cyclic hydrocarbons of petroleum.

1169. ———. [Action of Mixtures of Carbon Monoxide and Hydrogen or of Carbon Dioxide and Hydrogen on the Oxides of Iron.] Compt. rend., vol. 151, 1910, pp. 355–359; Chem. Abs., vol. 5, 1911, p. 2605.

Finely divided Fe_3O_4 was heated for 11 hr. at 500° in a mixture of 3 vol. of CO and 1 of H_2. The product is a mixture of C, FeO, and $Fe_{12}C$. Boiled with dilute H_2SO_4, it yields a mixture of CH_4 and H_2. With steam at 100° it also yields CH_4 and H_2, but at 650° the CH_4 disappears almost entirely, and CO_2 takes its place. Fe (coated on pumice) was heated to 1,250° in a stream of $2H_2+CO_2$; and the resulting gases, after washing with KOH, contained CO, 23.26%; H_2, 75.93%; CH_4, 0.15%; and N_2 (probably from the air), 1.27%. Fe_2O_3, heated in a mixture of equal volumes of CO and H_2 for 2 hr., yielded a product having properties similar to those of vaseline and the simple solid hydrocarbons. It is suggested that CO in the depths of the earth (either with or without H_2) has reacted with reducible oxides, forming carbides, which later, at temperatures below red heat, reacted with steam and formed the hydrocarbons issuing from the earth in volcanic regions or deposited as petroleum.

1170. GEBHARD, K., HANEMANN, H., AND SCHRADER, A. [Martensite System.] Arch. Eisenhüttenw., vol. 2, 1929, pp. 763–771; Chem. Abs., vol. 23, 1929, p. 3648.

Thermal and photomicrographic investigation of martensite, using electrolytic Fe and steels with C content ranging 0.06–1.75%. The heterogeneity of martensite is established, as well as the existence of a 2d metastable system of Fe–C alloys. Photomicrographs and a phase diagram of the martensite system are included. In the metastable martensite equilibrium only ϵ-Fe occurs up to about 0.1% C. 0.1–0.37% C, martensite consists of ϵ-Fe and heynite (θ-phase), while 0.37–0.9% C, heynite and hardenite (η-phase) are the constituents of martensite. With more than 0.9% C, a quenched steel contains hardenite and austenite, the austenite increasing as C increases. If the steel contains more than 1.1% C, the η-phase crystallizes from the γ-Fe immediately. If the equilibrium is not completely established, hardened steel contains austenite even with less than 0.9% C, and heynite even with more than 0.9% C.

1171. GEHRKE, —, AND SCHUFF, —. [Catalyst Plant and Synthesis Installation at Harnes.] FIAT Reel K–29, frames 7005–7028, 1938; PB 70,218.

Report on inspection of the catalyst plant and synthesis installation at Harnes. Proposals are made for the increase of the output and for eliminating certain existing deficiencies.

1172. GEISELER, —. Separation of Alcohols From Their Mixtures With Hydrocarbons. Scientific Contrib. 11, Laboratory, Merseburg Ammonia Plant, April 1943; Office Publication Board Rept., PB 870, 2 pp.

Following the work of H. P. Kaufmann on the separation of fatty acids by adsorption on silica gel, attempts were made to separate the mixture of alcohols and hydrocarbons arising from the Fischer-Tropsch medium-pressure synthesis. The method has for a basis the difference in the heats of wetting of alcohols and hydrocarbons. The process is covered by German Patent Applications I 72,811, IVd/12o, O.Z. 13570, and I 73,795, IV–d/12o, O.Z. 13,831. The alcohol-hydrocarbon mixture is mixed thoroughly with the active gel, which is then washed with a low-boiling hydrocarbon (petroleum ether, benzine, ligroin, benzol) to remove the adsorbed hydrocarbon, leaving the alcohol adsorbed on the gel. The alcohol is then recovered by being displaced by a highly polar liquid such as MeOH, EtOH, acetone, diethylether, etc., which likewise preferably remains attached to the gel. The gel is then regenerated by being treated with an excess (1:1,000) of hot gas (N_2, CO_2) at 150°. The process works best at room temperature and with a highly porous granular gel of 0.5–1 mm. size. The adsorption of the gel for alcohols embraces the whole range from C_1 to C_{20} and higher and becomes somewhat selective as the chains lengthen.

1173. GEMASSMER, —. Semiworks Experiments on the Oxo Process. Office Publication Board Rept., PB 853, 1942, 5 pp.

Oxo process was developed on pilot-plant scale according to the Maische procedure aided by the Fischer-synthesis catalyst. Describes plant, olefin product, catalyst, and gases.

1174. ———. Application of the Oxo Reaction to Olefinic Mineral Oil Products. Scientific Contrib. 8, Laboratory, Merseburg Ammonia Plant, April 1943; Office Publication Board Rept., PB 867, 1 p.

Possibility of using olefin products from various sources in the Oxo-reaction was investigated. Most of the materials used required no preliminary refining. Somewhat higher temperature was required than with olefins from the Fischer synthesis and conversion was also somewhat less (about 50%) than was to be expected from analysis of the samples. Hydrogenation was influenced by the S content and the boiling range of the oils; the higher boiling fractions hydrogenating the most satisfactorily. In those products, with which hydrogenation of the intermediate aldehydes did not occur smoothly, the Co_2C formed was still capable of reduction without difficulty to metallic Co, so that the incompletely hydrogenated products after separation of the catalyst were entirely free of metal. The complete hydrogenation to alcohol could then be carried out smoothly and without loss with the sulfide catalyst at remarkably low temperatures. The alcohols, recovered either by distillation or by esterification with boric acid, are water clear or pale yellow liquids of a pleasing, weakly aromatic odor having a low melting point and a remarkably high density due apparently to the cyclic structure. Chemically they behave similarly to other alcohols. The alcohol sulfates are good detergents, and their high solubility makes possible the use of members as high as C_{20} for the above purpose.

1175. GÉNIE CIVIL. [Underground Gasification of Coals in the U. S. S. R.] Vol. 122, No. 9, 1945, pp. 66–68.

Gives general review of the methods followed in Russia. (*See* abs. 1, 1628, 3698). The operation may be so varied that different types of gases for different specific uses can be produced as, for example, for the synthesis of NH_3 or hydrocarbons by the Fischer-Tropsch process. The average cost of gas produced in this way is about ⅓ that of the producer gas, and the cost of plant therefore about 60–70% of the cost of water-gas plant.

1176. GENIN, G. [Fluidization.] L'Industrie chimique, vol. 38, June and July 1951, pp. 157–163, 185–191.

History, theory and applications of fluidization are discussed. Its application to the petroleum industry, to the Fischer-Tropsch synthesis process, the catalytic manufacture of phthalic anhydride, the calcination of limestone, the reduction of minerals, the carbonization and gasification of coal, the manufacture of active C, and the classifying and drying of solid particles are reviewed. 34 refs. are given.

1177. GEORGES, P. [Substitute Liquid Fuels.] Jour. usines gaz, vol. 62, 1938, pp. 103–112; Chem. Abs., vol. 32, 1938, p. 7241.

Survey of the production of synthetic fuels according to Bergius and Fischer-Tropsch syntheses, and their development in important countries.

GERARD, F. W. *See* abs. 2769.

1178. GERASIMOV, Y. [Activities of Components of Austenite.] Acta physicochim. U. S. S. R., vol. 18, 1943, pp. 275–299; Chem. Abs., vol. 38, 1944, p. 5717.

Thermodynamic method is given for the calculation of the activities and free energies of a binary solution from the gas-solution equilibrium constants. The activities of the components Fe–C and Fe–Fe_3C at 800°–1,100° are calculated on the basis of the equilibrium constants between austenite and CO_2+CO. The values of K_p at 800°, 850°, and 900° K. are, respectively, 268.8 N_2, 510 N_2 and 962 N_2, where N_2 is the mole fraction of C in austenite. Since this means that the activity coefficient is practically unity, austenite can be considered a regular solution of a regular modification of carbide $Fe_3C(r)$ in γ-ferrite at 800°–1,100°. The free energy of formation of cementite is small and positive. The integral heats of solution of carbide and the solubilities of a "regular" carbide modification in Fe are given as: $Fe_3C(\beta)$ in $Fe(\gamma)$, 10,243 cal.; $Fe_3C(\beta)$ in a saturated solution, 5,000–7,000 cal. This latter modification is found to be less stable than cementite. The results indicate that the data of Bramley and Lord (*see* abs. 330) are probably vitiated by some sort of systematic error.

1179. GERDES, —. [Preparation of Water Gas From Brown Coal in the Pintsch-Hillebrand Generator.] Braunkohle, vol. 34, 1935, pp. 193–197, 216–219; Chem. Abs., vol. 30, 1936, p. 5762.

Describes new process using briquets and operating continuously without O_2. The process is particularly suitable for producing synthesis gas for the Fischer-Tropsch benzine synthesis. By utilizing the end gas from the benzine synthesis for heating the generator and with a briquet cost of 8 RM per ton the benzine can be produced for 8.3 pf. per kg.

1180. GERLACH, W., AND VON RENNENKAMPFF, J. [Magnetic Properties of Nickel Supersaturated With Carbon.] Naturwissenschaften, vol. 31, 1943, p. 96; Chem. Abs., vol. 37, 1943, p. 4999.

Anomalous decrease of saturation magnetization with increasing temperature in Ni supersaturated with C is restricted to the temperature range of room temperature <300°. The coercive force decreases normally between −200° and +50°, and remains constant from 50° up to 300°. In this range no saturation is reached, even at 3,000 oersteds. Numerous Curie points are in this range. The % remanence increases under 0°. This behavior is attributed to the facts that the alloy is a definite ferromagnetic substance of a Curie temperature about 50° plus a number of ferromagnetic Ni–C alloys of decreasing or indefinite C content, and that C separates and the alloy gradually approaches pure Ni with gradual rise of the Curie temperature and hardening. After separation of all the C the normal character reappears. After annealing at 600°, the temperature curve of magnetic saturation is normal.

1181. ———. [Magnetic Studies With Nickel–Carbon Alloys.] Ztschr. Elektrochem., vol. 49, 1943, pp. 200–203; Chem. Abs., vol. 37, 1943, p. 6507.

Curves are given for magnetization in low and in high fields, remanence, and coercive force as functions of temperature from −196° to 400° for Ni supersaturated with C. C in Ni is precipitated by heating at 600° leaving a material having the normal characteristics of Ni (abs. 1180).

GERNES, A. C. *See* abs. 2577.

GERSTEN, E. *See* abs. 2924, 2925, 2926.

GHOSH, J. C. *See* abs. 460, 461, 462.

1182. Ghosh, J. C., and Basak, N. G. Chromium Oxide as Catalyst Promoter for Fischer-Tropsch Synthesis at Medium Pressures. Petroleum, vol. 11, June 1948, pp. 131–132, 146; Chem. Abs., vol. 42, 1948, p. 5643.

Incorporation of Cr_2O_3 and Ce_2O_3 with a Co–Cu–ThO_2–kieselguhr catalyst, which has been claimed to have good activity, improves its quality in various respects. The catalyst, besides being reducible at lower temperature (237°–240°), functions steadily and yields, with cheap water gas at a pressure of 5 atm. and 205°, 160 gm. of hydrocarbons per m.^{3} of normal water gas. The space velocity is 570–600 cc. per hr. per cc. of catalyst in a 1-stage operation. Therefore, the synthesis of hydrocarbons by the Fischer-Tropsch process may be economically improved by the use of this catalyst.

1183. Ghosh, J. C., and Chakravarty, J. N. Dehydrogenation of Methanol and Formaldehyde With Copper as Catalyst. A Study of the Conditions of the Equilibrium in the System: $HCHO \rightleftharpoons CO+H_2$. Quart. Jour. Indian Chem. Soc., vol. 2, 1925, pp. 142–149; Chem. Abs., vol. 20, 1926, p. 860.

Equilibrium of the rection $CH_3OH \rightleftharpoons HCHO+H_2$ (I) and $HCHO \rightleftharpoons CO+H_2$ (II) were determined by a static method with Cu-pumice catalyst. For (I) the value found for K_p at 155° was 0.37 and at 205°, 0.65; these values differ widely from those calculated by a Nernst-type equation. For (II) the values of K_p from 155° to 340° (ranging from 0.032–2.20) were represented fairly well by the equation: $\log_{10}K_p = -(11{,}800/4.571T) + 1.75 \log_{10}T - 0.001T + 0.3$.

1184. Ghosh, J. C., and Chakravarty, K. M. Catalytic Preparation of a Gas Rich in Methane From a Mixture of Water Gas and Steam. Proc. Indian Sci. Cong., 15th Cong., 1928, pp. 148–149; Chem. Abs., vol. 25, 1931, p. 2835.

The authors have previously shown that a gas mixture containing CO and H_2 1 : 1 by vol. can be made to yield a fuel gas containing over 25% CH_4 if passed over suitable catalysts at temperatures 350°–450°. The efficiency and life of certain catalysts have now been increased very considerably by introducing steam in suitable proportions in the reacting gas mixture. The following reactions take place simultaneously on the catalyst surface: (1) $2CO \rightarrow CO_2+C$; (2) $C+H_2O \rightarrow CO+H_2$; (3) $CO+3H_2 \rightarrow CH_4+H_2O$; (4) $2CO+2H_2 \rightarrow CH_4+CO_2$. It is seen from (1) and (2) that CO reacts with steam, giving CO_2 and H_2. The H_2 so produced increases the ratio of H_2 to CO in the reacting gases and prolongs the life of the catalyst by preventing deposition of C. Catalysts (not mentioned) have been found which so regulate the rates of the reaction given above that the resulting fuel gases, after removal of CO_2, contain more than 50% CH_4.

1185. Ghosh, J. C., and Sastry, S. L. Chromium Oxide as Promoter in Catalysts for the Fischer-Tropsch Synthesis. Nature, vol. 156, 1945, p. 506; Fuel Abs., No. 5107, November 1945; Chem. Abs., vol. 40, 1946, p. 1083.

Economics of synthesis of hydrocarbons by the Fischer-Tropsch process may be improved by using (1) cheaper catalytic material, (2) water gas as such in place of enriched synthesis gas, and (3) medium pressures instead of atmospheric pressures. A cheap Fe-Cu catalyst prepared by Ghosh and Sen gave 86 gm. of hydrocarbons/m.^{3} of gas and has since been developed by Japanese investigators. The fact that Cr_2O_3 possesses very high adsorption for H at 200° has been taken advantage of in preparing a catalyst (Co 34%, Cu 4, ThO_2 2.3, Ce_2O_3 0.24, Cr_2O_3 4.6, remainder kieselguhr) which has been found to be remarkably steady, and yields, with water gas at a pressure of 5 atm. and 205°, 160 gm. of liquid hydrocarbons/m^3 with a space velocity of 600 cc./hr./cc. of catalyst.

1186. Ghosh, J. C., and Sen, S. Synthesis of Higher Paraffins From Water Gas. Use of Promoters for Activating Iron–Copper Catalyst. Jour. Indian Chem. Soc., vol. 12, 1935, pp. 53–62; Brennstoff-Chem., vol. 18, 1937, p. 161; Chem. Zentralb., 1935, I, p. 3496; Chem. Abs., vol. 29, 1935, p. 3903.

Investigation of possibility of activating an Fe–Cu catalyst by addition of Ni alone or by the simultaneous addition of Ni, Ce and Th. The catalyst was prepared from the nitrate and deposited on asbestos at as low a temperature as possible and subsequently impregnating with 0.5% K_2CO_3. The asbestos was one-half the amount of Fe and Cu. The effect of 1 and 2% of Ni and Ni, Ce and Th in the ratio of 8.03 : 0.13 : 0.95 on the Fe–Cu (4 : 1) catalyst was determined over a 14-hr. reaction period at 265° and a velocity of 0.65 l./hr. The yields of liquid hydrocarbons/m.^{3} of water gas were respectively 30, 45, and 80 gm.

1187. Ghosh, J. C., Basak, N. G., and Badami, G. N. Nickel-Thoria–Kieselguhr Catalyst for the Fischer-Tropsch Reaction. I. Current Sci., vol. 16, 1947, pp. 318–319, 353; British Abs., 1948, B, I, p. 190; 1949, B, II, p. 141.

Catalyst prepared by precipitation of Ni and Th carbonates on kieselguhr by addition of NH_4HCO_3 to a solution of the nitrates in presence of excess of CO_2, and subsequent reduction in H_2, first at 500° and then at 300°–350° (for 6 hr. in each case), gave 147.5 gm. hydrocarbons other than CH_4/m.^{3} of synthesis gas with a space velocity of 0.90 l./hr./gm. of Ni.

1188. ———. Nickel–Thoria–Kieselguhr (100 : 18 : 100) Catalyst for the Fischer-Tropsch Reaction. II. Current Sci., vol. 16, 1947, p. 353; British Abs., 1949, B, II, p. 141; Chem. Abs., vol. 43, 1949, p. 3167.

By the use of water gas (CO : H_2=1 : 1) instead of H_2-enriched synthesis gas (CO : H_2=1 : 2), it has been found that this catalyst gives (*a*) yields of hydrocarbons comparable with those produced from synthesis gas, (*b*) gaseous preponderating over liquid hydrocarbons, and (*c*) lower yields of CH_4 which remain almost constant with increasing space velocity. The experiments were carried out at 195° and 1 atm., and a maximum yield (125 gm./m.^{3} of gas) was obtained with a space velocity of 0.9 l./gm. of Ni. The catalyst used is described in abs. 1187.

1189. Ghosh, J. C., Basak, N. G., and Venkatesan, C. Nickel-Thoria-Kieselguhr (100 : 18 : 100) Catalyst for the Fischer-Tropsch Synthesis at Medium Pressure. III. Current Sci., vol. 16, 1947, p. 377; Chem. Abs., vol. 43, 1949, p. 3167.

At 70 p. s. i. with synthesis gas, as well as water gas, the best reaction takes place at 205°. When synthesis gas is used, the yield of CH_4 is high. With water gas the yield of CH_4 goes down with a corresponding increase of gaseous and liquid hydrocarbons.

1190. Ghosh, J. C., Chakravarty, K. M., and Bakshi, J. B. [Catalytic Formation of Methane From Carbon Dioxide and Hydrogen: Simultaneous Acceleration of the Water Gas and Armstrong-Hilditch Reactions.] Ztschr. Elektrochem., vol. 37, 1931, pp. 775–779; Chem. Abs., vol. 26, 1932, p. 648.

Catalysts I, II and III were prepared respectively by impregnating pumice with nitrate solutions, drying in air at 110°, then heating for 16 hr. at 300° in pure H_2. The weights of catalyst used were 0.6440, 0.7100, 0.6565 gm., the densities after reduction 0.4155, 0.4438, 0.4646, % Ni 8.882, 8.433, 8.030, % Ce —, 0.0687, 0.1308, % Th —, 4.978, 9.479, and % pumice 91.11, 86.52, 82.37, respectively for I, II, and III. The reaction tube was maintained at 405° and the catalyst at 471°. Equal volumes of H_2 and CO, saturated with water vapor, were admitted at constant velocity. With catalyst I, reactions (1) $CO+H_2=C+H_2O$ and (2) $CO_2+2H_2=C+2H_2O$ did not take part because no free C was deposited in disagreement with Randall and Gerbard (*see* abs. 2769). Catalyst I lost its CH_4-forming properties with use but was still capable of promoting the water-gas reaction. Catalysts II and III showed no loss of CH_4-forming properties. After 180 l. had passed, II gave 32.02% CO_2, 9.65% CO, 25.58% CH_4, 22.52% H_2, 10.23% H_2O from 44.48% CO, 44.48% H_2, and 11.03% H_2O. II gave after 190 l., 36.19% CO_2 5.43% CO, 30.12% CH_4, 17.38%. H_2, 10.78% H_2O from 44.78% CO, 44.78% H_2 and 10.46% H_2O.

1191. ———. [Simultaneous Determination of the Equilibrium Constants of the Reactions $CO+H_2O \rightleftharpoons CO_2+H_2$; $2CO+2H_2 \rightleftharpoons CO_2+CH_4$; $CO+3H_2 \rightleftharpoons CH_4+H_2O$; $CO_2+4H_2 \rightleftharpoons CH_4+2H_2O$ by Using Activated Nickel Catalysts.] Ztschr. anorg. Chem., vol. 217, 1934, pp. 277–283; Chem. Abs., vol. 28, 1934, p. 6613.

Experimental arrangement was similar to that previously described (*see* abs. 1190) but the gas mixture was passed much more slowly over the Ni–ThO_2–CeO_2 catalyst to insure that the temperature of the gases should be the same as that of the furnace. The required equilibrium constants were determined at temperatures 400°–490°.

1192. Ghosh, J. C., Sastri, M. V. C., and Kini, K. A. Adsorption of Hydrogen and Carbon Monoxide and Their Mixtures on Fischer-Tropsch Catalysts. I and II. Current Sci., vol. 15, 1946, pp. 282–283; Chem. Abs., vol, 41, 1947, p. 1907.

Adsorption of H_2 and CO, both as pure gases and as mixtures, was studied on a catalyst of the following composition: Co 34.2, Cu 4.08, ThO_2 2.33, Ce_2O_3 0.24% on kieselguhr. In mixtures the presence of 1 gas promoted the adsorption of the other, even at temperatures considerably below those where the velocity of reaction becomes perceptible. The increase of adsorption with H_2 was conspicuous, even at 25°. The adsorption was measured volumetrically and is tabulated in terms of the volume adsorbed by 9.41 gm. of catalyst from the pure gas from 1 : 1, 1 : 2, and 2 : 1 mixtures of H_2 and CO at temperatures up to 178°. The logs of the values for the rate of adsorption at constant pressure when plotted against the logs of the corresponding volumes adsorbed, gave straight lines that were parallel for different pressures at a given temperature. The results suggested $u=kP/V^n$ as the empirical relation between the rate of adsorption, the pressure and the amount of adsorption, where u= rate of adsorption in cc./min., P=pressure, V=volume adsorbed, and n and k are constants.

1193. ———. Mixed Adsorption of Hydrogen and Carbon Monoxide on Fischer-Tropsch Catalysts. Research, vol. 3, 1950, p. 584.

Previously (*see* abs. 1192) it was found that on a Fischer-Tropsch catalyst (A) containing 34% Co, 4% Cu, 2.33% ThO_2, 0.24% Ce_2O_3 and the rest kieselguhr, the adsorption of H_2 from 1 CO : 1 H_2 and 1 CO : 2 H_2 mixtures, at temperatures 25°–97° and mixed pressures below 76 cm., was greater than from pure gas at equivalent pressures. At the same time, there was a suppression of CO adsorption from the mixtures. The addition of 4% Cr_2O_3 to (A) (*see* abs. 1182) caused marked improvement in the yield of gasoline and facilitated the use of water gas (1 CO : 1 H_2) without the usual enrichment of H_2. It also increased the adsorption of pure CO at all the temperatures studied (25°–97°) but suppressed that of pure H_2 up to 76° and increased it at higher temperatures. The adsorption of CO at higher partial pressures was found to be greater from the 1 CO : 2 H_2 than from the 1 : 1 mixture, while the reverse was true of H_2 adsorption. That is, adsorption of either gas was greater from that mixture in which its concentration was lower. On both catalysts it was observed that the adsorption of each constituent began to increase at much lower temperatures in presence of the other gas than in its absence. These facts point to the possibility of progressive formation of a CO–H complex on the surface of the catalyst. If the simultaneous adsorptions of the constituent gases were plotted against each other the "isotherms" so obtained tended to become linear at the higher temperatures, and for every 2 cc. increase in CO adsorption that of H_2 increased by nearly 1 cc. This again supports CO–H complex formation. It therefore appears that the chemisorbed CO–H complex, rather than the Co carbide, may be the intermediate in Fischer-Tropsch synthesis by catalyst (B) Cr_2O_3+(A).

1193a. ———. Adsorption of Hydrogen and Carbon Monoxide and Their Mixtures by Cobalt Fischer-Tropsch Catalysts. Ind. Eng. Chem., vol. 44, 1952, pp. 2,463–2,470.

In order to gain an insight into the nature of the reactive substrate in Fischer-Tropsch synthesis, the adsorption of H_2 and CO was studied at various temperatures from the pure gases as well as from their mixtures on 2 Co catalysts, 1 of which contained Cr_2O_3 as a promoter. Both gases underwent activated adsorption at fairly low temperatures. Cr_2O_3 enhanced the amounts and rates of adsorption of both, lowered their activation energies of adsorption, and thus acted as a promoter. Experiments were conducted with $1CO+1H_2$ and $1CO+2H_2$ mixtures, using a thermal conductivity meter for analysis. The adsorption of each constituent was found to be markedly influenced by the presence of the other. Kinetic studies revealed that the high initial adsorption of H_2 was followed by a partial replacement of adsorbed H_2 by CO. Near the minimum temperature of appreciable reaction, the concurrent adsorptions of CO and H_2 increased with the partial pressures in the ratio of $2CO:1H_2$. The observations reported in this paper point to the formation of chemisorbed CO–H_2 complexes as 1 of the 1st steps in the transformation of the substrate. The results are also in correlation with reaction-performance data previously reported on these catalysts.

1194. Ghosh, J. C., Sastri, M. V. C., and Vedaraman, S. Adsorption Studies on Methanol-Synthesis Catalysts. I. Adsorption of Carbon Monoxide and Hydrogen on Zinc Oxide–Chromium Oxide Mixture. Current Sci., vol. 19, 1950, p. 342. Chem. Abs., vol. 45, 1951, p. 7406.

Temperature range studied was 50°–200° for CO and up to 250° for H_2. The adsorption isobars of CO at pressures below 1 atm. show 2 maxima, at 52° and at 178°. The activation energy is 5–8.5 kcal., and the heat is 6 kcal. for 0.9 cc. adsorption/gm. For H_2, activated adsorption is observed at the lowest temperature; the heat is 10 kcal. for 1.30 cc. adsorption/gm. and the energy of activation is 8.5 kcal. for 1.19 cc. adsorption/gm. at 37 cm. pressure. The maximum adsorption is at 204°.

Gibson, E. J. *See* abs. 1131a.

Giesen, —. *See* abs. 3703, 3704.

Giessen, A. *See* abs. 407.

1195. Gifford, A. P., Rock, S. M., and Comaford, D. J. Mass-Spectrometer Analysis of Alcohols and Other Oxygenated Derivatives. Anal. Chem., vol. 21, No. 9, 1949, pp. 1026–1032.

Mass-spectrometer analysis of alcohols or mixtures of oxygenated compounds containing them has been difficult because of strong sorption tendencies of these materials. In an examination of the erratic behavior of the alcohol spectra, it was found possible to minimize the effect of these difficulties by minor changes in the mass-spectrometer sample inlet system sufficient to permit analysis of synthetic mixtures of oxygenated compounds. It is shown by alternate analyses of known mixtures widely varying in concentration of light and heavy alcohols that the different materials can be separated in the mixture spectra and that any effect of 1 sample upon a succeeding one is insignificant. Analysis of a synthetic mixture of the 4 butanol isomers shows that alcohol isomers are also readily resolved. That the errors in the analyses are relatively small demonstrates that sufficient accuracy can be obtained in the separation of alcohols to meet normal analytical needs. Analysis of the 4 butanol isomers mixed with water demonstrates that the presence of water does not prevent precise results and that water can be determined accurately. Analyses of complex mixtures show that other oxygenated compounds can be determined with adequate precision in the presence of alcohols and water.

GILFERT, W. *See* abs. 1820, 1821, 1822.

1196. GILLET, A. [Synthesis of Fuel Oils and Lubricating Oils From Carbon Monoxide and Hydrogen at Ordinary Pressure.] Rev. univ. mines. vol. 11, 1935, pp. 180–184; Chem. Abs. vol. 29, 1935, p. 4561.

Two principal methods of industrial transformation of coal into oil are the Fischer and the Bergius processes. The former seems to be the more advantageous because it operates at ordinary pressure with simple apparatus made of sheet Fe and because it permits the manufacture, at the same time, of high-grade lubricating oils. The yield depends to a high degree on the catalysts used. The most effective are Fe with additions of Ni, Mn, Al, Th, Co, singly or several together. A table shows the yield in gm. of oil per m³ of $CO+2H_2$ and time required for an efficiency of 80%. The reasons for the deterioration of catalysts are discussed. As the transformation into fuel oil sets free about 600 cal. per m.³, means must be provided to carry away this heat quickly enough to maintain reasonably constant temperature. The products with a Co catalyst are usually 100–120 gm. of liquid hydrocarbons (180 gm. theoretically). The process and products are described.

1197. GILLILAND, E. R. Techniques of Contacting Fluids and Solids. 5th Westman Memorial Lecture; Canadian Chem. Process Ind., vol. 34, 1950, pp. 632–640.

Discusses techniques of fixed, moving, and fluidized beds in industrial operations. The greatly improved heat-transfer characteristics in the fluidized bed are emphasized; it merits consideration for any reaction in which (1) temperature control within the reaction or (2) heat transfer to and from the reaction vessel, or (3) frequent, alternate cycles with the catalyst are necessary.

——. *See* abs. 2110.

GILMONT, P. *See* abs. 262a.

1198. GILMORE, R. E. Carbonization of Canadian Fuels. Canadian Chem. and Met., vol. 10, 1926, pp. 31–34, 51–54, 85–87, 140–144.

Application of high- and low-temperature carbonization to wood, peat and other classes of Canadian fuels; gasoline and substitute fuels in Canada, with special reference to synthetic MeOH and synthol.

1199. GINSBERG, I. Wood Alcohol From Water Gas. Am. Gas. Jour. vol. 122, 1925, pp. 461–462.

Review of process developed by Patart and Badische, with a sketch of the apparatus and a description of the catalyst. It generally consists of a mixture of Zn and ZnO, with traces of Cd and CdO in admixture with a commercial Cu powder. Best results are obtained at a temperature of 220°–300° and 150–250 atm. The yield per hr. reaches as high as 100 cc. of MeOH per vol. of catalyst of 200 cc. This product is relatively very pure.

1200. GIORDANI, C. [Gasoline Substitutes.] Jour. usines gaz, vol. 61, 1937, pp. 170–175, 196–202, 229–233; Chem. Abs., vol. 31, 1937, p. 5537.

Present state of development of the coal hydrogenation and Fischer-Tropsch processes is comprehensively summarized. Yields and cost figures are included.

1201. ———. [Liquid Substitute Fuels.] Acqua e gas, vol. 27, Feb. 16, 1938, pp. 37–46; Chem. Zentralb., II, 1938, p. 1164.

Fischer and Bergius processes are discussed in relation to the production of high-octane fuel and high-grade lubricants under war demands.

GIORDANO, I. *See* abs. 2558.

GIRARD, J. *See* abs. 553.

1202. GITTIG, M. Exothermic Reaction Techniques. Petrol. Processing, vol. 5, No. 10, 1950, pp. 1080–1082.

Exothermic reaction techniques are classified and their application for heat-removal and control purposes in commercial chemical processes reviewed. The use of fluidized solids reactors in the Fischer-Tropsch process has served to greatly reduce the total volume of cooling surface required. Since a rocket motor is essentially an exorthermic reactor, the application of the same principle in chemical-process reactor design is considered a possibility. The injection of various fluids as temperature-control mediums in exorthermic gas reactions has been patented.

1203. GIVAUDON, —. [Industrial Reactions of Methane.] Assoc. franç. techn, pétrole, Conf. 1945, pp. 22–50; Chaleur et ind., vol. 26, 1945, p. 43D.

Sources of CH_4 and its conversion into CO and H_2 are discussed. Various processes are outlined: Harnes, Grande-Paroisse, Padovani, Soc. belge. de l'azote. The possibility of introducing CH_4 directly into the Fischer hydrogenation is considered. The decomposition of CH_4 into C and H_2 and carbon black, the production of C_2H_2, and its use in the plastics industry are treated.

GIVAUDON, J. *See* abs. 1604.

GIVEN, P. H. *See* abs. 3397.

GIVENS, J. W. *See* abs. 180.

GLAESSNER, A. *See* abs. 168.

GLENN, R. D. *See* abs. 2178.

1204. GLOOR, W. E. Notes on the Development of Protective Coatings in Germany. Am. Paint Jour., vol. 30, No. 12, 1945, pp. 95, 98, 100, 102, 104, 106; Chem. Abs., vol. 40, 1946, p. 1047.

New placticizer used with cellulose acetate was the triethylene glycol ester of long-chain fatty acids from Fischer-Tropsch synthesis.

1205. GLUUD, W., AND SCHÖNFELDER, R. [Increasing the Activity of Iron (Ammonia) Catalysts.] Ber. Gesell. Kohlentech., vol. 3, 1930, pp. 96–99; Chem. Abs. vol. 25, 1931, p. 3779.

Catalyst containing Fe is treated with CO to form Fe_2C, which is then reduced by H_2.

1206. GLUUD, W., OTTO, K. V., AND RITTER, H. [Iron Carbide by Reduction of Iron Oxide With Carbon Monoxide at Low Temperature.] Ber. Gesell. Kohlentech., vol. 3, No. 1, 1929, pp. 40–51; Ber. deut. chem. Gesell., vol. 62B, 1929, pp. 2483–2485; Chem. Abs., vol. 24, 1930, p. 561.

CO is passed over Fe_3O_4 at 275° and the C content determined periodically. Graphic treatment of the data gives values for dissolved C which, when subtracted from the totals, give values which become constant after 20 hr. This value corresponds to Fe_2C. Removal of C by H_2 gives the same values. The data of Fischer and Bahr (*see* abs. 973), similarly interpreted, give the same results.

GODDIN, C. S. *See* abs. 810.

1207. GODDIN, C. S., AND THORNTON, D. P. Low-Temperature Carbonization of Coal Produced Most of Japs' Synthetic Oil. Petrol. Processing, vol. 3, 1948, pp. 121–122, 124–125, 127, 130–131; Chem. Abs., vol. 42, 1948, p. 9112.

This article reviewing Japanese efforts to synthesize liquid fuels from coal is based on the report of the U. S. Naval Technical Mission to Japan. Report X–38 (N)–7, Japanese Fuels and Lubricants, Progress in the Synthesis of Liquid Fuels from Coal, PB 58,701.

GOECKE, O. *See* abs. 2927.

1208. GOEPFERT, O. [Deterioration of Fischer-Synthesis Catalysts and Participation of Methane in This Synthesis.] Compt. rend., vol. 224, 1947, pp. 340–341; Chem. Abs., vol. 41, 1947, p. 3739.

Experimentally it is observed that mixtures of C_2H_6 and H_2 react on a Ni-kieselguhr catalyst at 150°–160° C. to form CH_4. The reaction does not proceed simply according to the equation: (1) $C_2H_6+H_2 \rightarrow 2\ CH_4$. Instead, more C_2H_6 than H_2 is used. The results can be explained by means of an additional reaction: (2) $2\ C_2H_6 \rightarrow 3\ CH_4+C$ taking place simultaneously with (1). It is claimed that reaction (2) indicates the capacity of the catalyst to dissociate CH_4 according to the mechanism: (3) $CH_4\ (ads) \rightleftharpoons CH_3(ads)+H(ads) \rightleftharpoons CH_2(ads)+2\ H(ads) \rightleftharpoons CH(ads)+3\ H(ads) \rightleftharpoons C(ads)+4\ H(ads)$. These results indicate merely that carbides (possibly bulk carbides) can be formed by the action of C_2H_6 on Ni.

1209. GOERING. —. Synthesis in the Liquid Phase. High-Pressure Experiments, Ludwigshafen · 558, Mar. 11, 1943. Bureau of Mines Transl. T–433, Jan. 1948, 7 pp.

Patent history of the process beginning with Pier's German Patent 630,824, and covering a number of I. G. Farbenindustrie applications and patents under the names of Michael, Duftschmidt, Linckh, and others.

1210. GOESCHEL, H. [High-Tension Technic in the Field of Motor-Fuel Recovery Plants.] Elektrotech. Ztschr., vol. 58, 1937, pp. 1282–1287, 1317–1320; Coal Carbonisation, vol. 4, 1938, p. 63; Chem. Abs., vol. 32, 1938, p. 3575.

Relative situations of petroleum and synthetic motor fuels (the major processes for liquid fuel production from coal) are described and discussed from an electrical engineering point of view for plant equipment and operation. The nature of the problems imposed upon the electrical industry is discussed, particularly as regards making maximum use of standard equipment in the interests of economy and rapid construction. Security of supply and safety against explosion risk are primary requirements, and the necessary arrangements in networks, distribution circuits, motors, switchgear, lighting and other equipment are explained. Pressure and vacuum pumps and compressors are required in sizes up to several thousand kw. Available types of motors are discussed. Application of electricity to process control is exemplified and illustrated in the case of the catalytic chambers of the Fischer-Tropsch process.

GOFMAN, E. *See* abs. 1664.

GOHR, E. J. *See* abs. 2347.

GOLDEN, P. L. *See* abs. 1370, 3215, 3294.

1211. GOLDSTEIN, R. F. Petroleum Chemicals Reviewed. III. The Fischer-Tropsch Reaction. Petrol. Times, vol. 51, 1947, pp. 892–893.

Review with particular emphasis on the Hydrocol process and its economic significance. As regards the production of chemicals, it is remarked that this new source of aliphatic chemicals is going to have a serious effect upon the plants already producing aliphatics from petroleum.

1212. ———. Petroleum Chemicals Reviewed. Petrol. Times, vol. 52, Nov. 19, 1948, p. 1016.

Probable future development and expansion of petroleum chemicals are reviewed. Present trends indicate that the period of cheap chemical raw materials has passed. Propane and butane are more valuable as domestic fuels than as raw materials for aliphatics. Byproducts of synthetic plants such as Fischer-Tropsch may prove an important source. NH_3 is made from H_2 with natural gas as the source. For MeOH the natural gas is converted to a synthesis gas $CO+2H_2$, which is converted to MeOH by catalytic reaction at high temperature and pressure. Under the head of new products the manufacture of acrolein from petroleum and the Oxo reaction are discussed. The latter gives normal or branch-chain aldehydes by addition of CO and H_2 to an olefinic double bond. Acids and alcohols can be obtained from the aldehydes.

1213. ———. The Petroleum Chemicals Industry. John Wiley & Sons, New York, 1950, 449 pp.

Survey of literature dealing with initiation and development of the petroleum-chemicals industry. Chapters 2–5 deal with the chemistry of the paraffins (chapter 2 treats particularly of the synthesis and reactions of $CO–H_2$ mixtures as exemplified by the Fischer-Tropsch, the Hydrocol, and the Synol processes). Chapters 6–10 treat of the manufacture of olefins and the chemical developments based on them (chapter 10 discusses briefly the reaction of CO and H_2 with olefins, the so-called Oxo process). The manufacture of diolefins, naphthenes, aromatics and acetylene is discussed in chapters 11–14.

1214. GOLDSTEIN, R. F., AND SNOWDEN, F. F. Oxo Synthesis. Interrogation of Dr. Roelen. BIOS Interrogation Rept. 736, May 1946, 6 pp., PB 81,967.

1215. GOLUMBIC, N. Review of Fischer-Tropsch and Related Processes for Synthetic Liquid Fuel Production. Bureau of Mines Inf. Circ. 7366, 1946, 24 pp.

Review with emphasis on the more recent developments, covering historical, industrial, and process development, mechanism of the Fischer-Tropsch process, production of synthesis gas, manufacture of catalysts (Ni, Co, Fe, and Ru), properties of the primary synthesis products, and their treatment.

1216. ———. Some Chemicals From Synthetic Liquid Fuels Processes. Bureau of Mines Rept. of Investigations 4467, 1949, 58 pp.

Review of some available literature and experimental results of 2 synthetic liquid fuels processes now under investigation; presents summary of information regarding relative amounts of various industrially valuable chemical products thus produced. Gives brief description of the Fischer-Tropsch and related processes with emphasis on the effect of the important variables, catalyst, pressure, temperature and H_2: CO ratio upon the composition of the product. Enumerates byproducts and chemicals obtainable from hydrogenation of CO. Also reviews the work accomplished on the hydrogenation of typical United States coals, including a description of the liquid-phase hydrogenation assay procedure and summarized results of characterization of the oils produced during the hydrogenation of Pittsburgh-seam (Bruceton) coal under various conditions in the Bureau of Mines experimental plant. Important byproducts from the Fischer-Tropsch synthesis are water-soluble organic chemicals, such as EtOH, acetic acid, and acetone. These products will be available in large enough quantities to have a tremendous economic effect upon established sources and uses. They may become the principal source of many basic, organic chemicals, particularly those used in cellulose plastics and fibers, acetate rayon, pharmaceutical, and aliphatic solvent industries. Another potential source of important organic chemicals is the production of high-boiling alcohols from the Oxo and Synol processes. Oil from the liquid-phase hydrogenation of coal is an important source of organic chemicals of commercial value, such as tar acids for plastics, tar bases for pharmaceuticals, and benzene, toluene, and xylene for explosives manufacture and solvents.

———. *See* abs. 3296, 3297.

1217. Golumbic, N., Anderson, H. C., and Grass, R. C. Revised Bibliography of Bureau of Mines Investigations on the Production of Liquid Fuels From Oil Shale, Coal, Lignite, and Natural Gas to 1949. Bureau of Mines Inf. Circ. 7534, 1949, 53 pp.

Includes Government publications written by the Bureau of Mines staff for the technical press and reports of work done jointly with States, colleges, and industries. (*See* abs. 923.)

Gondzik, J. *See* abs. 1972.

1218. Goodeve, C., and Jack, K. H. Kinetics of Nitrogen Evolution From an Iron-Nitrogen Interstitial Alloy. Disc., Faraday Soc., No. 4, 1948, pp. 82–91; Chem. Abs., vol. 43, 1949, p. 4933.

Rate of N evolution from ϵ–Fe nitride at 350°–500° is given by a 2d-order equation with respect to interstitial N concentration and is associated with an activation energy of 42,100±1,400 cal. per gm. mol. The evolution rate of N atoms per 100 Fe atoms per sec. is given as $r=2z\,(10^2/A)=(10^2\,Nc\pi n/A)\,e^{-E/RT}$, where A is the number of Fe atoms in the nitride particle. The approximate value for the successful collisions w is taken as 3 A. From the known structure of ϵ–nitride and the observed particle diameter N, n and A are known. At 450°, the values are $c=1.05\times10^5$ cm. per sec.; $N=1.9\times10^6$; $n=3.8\times10^{14}$; $A=2.3\times10^{12}$. Thus, at 450°, r ranges from 0.7–4.3×10^{-3} with a most probable value of 1.8×10^{-3} N atoms per 100 Fe atoms per sec. The velocity of diffusion of N atoms to the surface is at least 10^4 times as rapid as the rate-determining process. The rate-determining stage of the reaction is considered the combination of N atom pairs at the solid surface. By calculation of the collision frequency on the assumption that this surface reaction behaves as in a 2-dimensional gas, the correct order of magnitude for the absolute reaction rate is predicted.

Goodman, J. B. *See* abs. 2576, 2577.

1219. Gordon, A. S. Uncatalyzed Reaction of Natural Gas and Steam. Ind. Eng. Chem., vol. 38, 1946, pp. 718–720: Chem. Abs., vol. 40, 1946, p. 5545.

Uncatalyzed reaction of natural gas with steam has been studied 1,225°–1,516° with steam : natural-gas ratios of 1.5 : 5, and time of contact 0.21–4.6 sec. Even at high temperatures, long contact times, and steam : natural gas ratio of 5 there is some carbonization of the natural gas. The extent of carbonization is shown to be a function of the ratio of steam to natural gas, and to vary erratically with temperature and time of contact. As the temperature is increased, the % of natural gas undecomposed in a single pass through the furnace becomes less dependent on contact time (in the range of contact times studied), until at about 1500° there is little or no effect. At any temperature the % of undecomposed gas shows little if any dependence on the ratio of steam to natural gas. The application of this reaction to the production of a mixture of H_2 and CO for synthesis gas is pointed out.

1220. ———. Mechanism and Kinetics of the Thermal Decomposition of Methane in a Flowing System in the Region 1,000°–1,075° C. Jour. Am. Chem. Soc., vol. 70, 1948, pp. 395–401.

Mechanism and kinetics of the thermal decomposition of CH_4 have been studied in a porcelain reaction vessel using a flow system at 1,000°–1,075°. The data were treated in accordance with the assumption that the reaction was unimolecular and homogeneous as had been reported previously for a static system up to 850°. The reaction constants were found to increase with increasing decomposition which indicates a reaction less than first order or autocatalytic. The latter hypothesis was tested by adding separately small % of the various product gases to the original CH_4. It was shown that 0.72% C_2H_2 increased the reaction rate 2 to 2½ times its original value. The catalysis may be a homogeneous direct attack on CH_4. The addition of 1% of C_2H_4 likewise increased the reaction to about the same extent, but this is probably due to the C_2H_2 which is rapidly formed from the C_2H_4. Addition of 2% H_2 to the reactant CH_4 also gives a 20–30% increase in reaction rate with a concurrent increase in C_2H_2 content, which accounts for at least part of the effect on the reaction rates. Larger concentrates of H_2 had previously been shown markedly to slow the rate of decomposition. By increasing the surface : volume ratio about fourfold, the rate of decomposition is about 2½ times as great, part of the effect arising from an increased % of C_2H_2.

1220a. ———. Reaction Between Methane and Steam in the Temperature Region 1,000°–1,100°. Ind. Eng. Chem., vol. 44, 1952, pp. 1857–1859; Chem. Abs., vol. 46, 1952, p. 11,637.

The present work is an outgrowth of a study of the uncatalyzed steam-natural gas reaction at temperatures 1,200°–1,500° and a total pressure of 1 atmosphere. Between 1,000°–1,100° and 1 atmosphere the results of this work show that the reaction between CH_4 and steam is probably a combination of the decomposition of CH_4 followed by the steam-carbon reaction. Until C is formed as a result of the decomposition, steam behaves as an inert gas. Production of synthesis gas from CH_4 and steam for the Fischer-Tropsch process proceeds smoothly at about 900° on a Ni catalyst. Without an efficient catalyst, at considerably higher temperatures, there is no problem of decomposing CH_4, but gasification of the resulting C is so slow that an efficient catalyst for this reaction would be required to make the reaction economically feasible.

1221. Gordon, K. Development of Hydrogenation and Fischer-Tropsch Processes in Germany. Jour. Inst. Petrol., vol. 33, 1947, pp. 469–490; Chem. Abs., vol 42, 1948, p. 2417.

This paper, presented at a meeting of the Institute of Petroleum in May 1947, summarizes what has been done in Germany on the hydrogenation and Fischer-Tropsch processes and compares briefly the techniques adopted in both Britain and Germany.

1222. ———. Hydrogenation in the Fuel and Chemical Industries. Jour. Inst. Fuel, vol. 21, Dec. 1947, pp. 53–61; Petroleum (London), vol. 10, 1947, pp. 244–246, 262; vol. 11, 1948, pp. 16–17, 35–38; Gas World, vol. 127, 1947, pp. 556–558; Chem. Abs., vol. 42, 1948, p. 2077.

Melchett lecture for 1947 first deals with the manufacture of H_2 and of mixtures with N_2 required for making synthetic NH_3, and with CO for making synthetic MeOH. Refers to the manufacture of synthetic fuels by the Fischer-Tropsch process and to the reactions between olefins, CO, and H_2, according to the work of Roelen and Reppe. Considers a number of different types of reaction involving hydrogenation and describes analogous operations as carried out in the petroleum, fuel, and chemical industries. Gives account of the manufacture of aviation fuel.

1223. ———. Production of Petroleum by Synthetic Methods. Gas World, vol. 127, 1947, p. 78; Chem. Age, vol. 57, 1947, pp. 221–222, 269–270.

Paper presented at St. Andrew's symposium. Discusses 2 main methods for the production of gasoline—coal hydrogenation and Fischer-Tropsch synthesis. Coal has been used at Billingham as the raw material; it has now been superseded by creosote oil and tar, as the coal caused great abrasion of the plant and during the war the plant could be more easily and safely shut down in case of air attack. When coal is used, it is first washed by flotation, then powdered and mixed with oil to give a paste from which the oil may be recovered by recycling. Owing to the nature of coal, about 5% avoids hydrogenation, a figure that may be increased if the coal is alkaline. To obtain more complete hydrogenation it is customary to add to the charge a small excess of HCl in the form of NH_4Cl. The ideal method of hydrogenating coal is to use 4 stages, although a satisfactory product may be obtained using 2, while at Billingham 3 stages are employed. In the initial stages the catalysts employed are Sn oxide and Fe sulfide, and in the final stage WS_2. The product from coal or tar hydrogenation is purely hydrocarbon in character in the fraction boiling up to 180°; above this temperature phenols and basic substances are obtained. The average yield of gasoline from bituminous coal is about 50%, although this figure will be slightly increased if the gasoline is for motor fuel and decreased if for aviation fuel. German annual output during the was was about 4,000,000 tons, while that at Billingham and Heysham was 500,000 tons. Gasoline obtained by this method has an octane number of 80, which can be increased to 95 by addition of Pb, and to 100 by addition of iso-octane. The economic prospects for this process are less favorable than they were 20 yr. ago mainly due to the increased costs of coal and labor, coupled with the fact that the gasoline sold today is of a higher quality than formerly.

1224. ———. Report on the Petroleum and Synthetic Oil Industry of Germany. BIOS Overall Rept. 1, 1947, 134 pp., PB 88,981s.

Divided under the following headings: Carbonization and gasification of coal; hydrogenation processes; Fischer-Tropsch process: crude-oil production; petroleum refining; lubricating-oil production; and testing and evaluation of products. The report comprehensively reviews the oil situation during the war, the sources of liquid fuels, and the contribution thereto made by coal-oil processes. Oil from various sources reached a maximum output of 6,930,000 tons in April 1944, but fell rapidly by the end of August to 120,000 tons. Hydrogenation was the largest oil producer (up to 3,250,000 tons); Fischer-Tropsch was less important (up to 585,000 tons); while petroleum, coal-tar distillation, and benzol showed, respectively, 1,770,000, 945,000, and 380,000 tons. Costs of synthetic fuels were entirely uneconomic compared with natural petroleum. Translated to present-day costs in Great Britain, the production costs of hydrogasoline from coal and tar respectively were 27.5 d. and 21.9 d. per gal., and for Fischer-Tropsch primary product 27.1 d. The processes for refining petroleum and for producing high-octane motor and aviation fuels were similar to those in general use but had not reached as high a state of development as in the allied countries.

1225. Gordon, W. R. South African Coal Industry. Canadian Min. Jour., vol. 70, No. 5, 1949, pp. 76–79.

Summary of report of the Coal Commission and of annual report for the Fuel Research Board for 1947 and a review of the coal trade are presented. Some discussion of proposed oil-from-coal plant now licensed to be erected at Vereeniging. The Hydrocol process is to be employed. One of the major improvements in this new plant is the use of "fluidized" Fe as the catalyst. The plant will have a capacity of 76,000,000 gal. of liquid fuel per year, including 10,000,000 gal. of diesel oil. The coals to be utilized are for the most part low-grade. It has not yet been definitely ascertained whether or not such coals will be satisfactory for making synthesis gas by gasification to be converted into liquid fuel.

Goss, W. H. *See* abs. 2176, 2177.

1226. Göthel, —. Grenzflachen-Katalyse. Kröger, editor, Hirzel, Leipzig, 1933, p. 67.

It was found that the electrical conductivity of various powdered catalysts varied during the Fischer synthesis in such a way as to indicate the progressive formation of carbide.

1227. Gotoh, Y. [Reduction of Ferric Oxide by Hydrogen and Oxidation of Metallic Iron Reduced From Ferric Oxide.] Mem. Ryojun Coll. Eng., Inouye Commemoration, vol. 1934, pp. 393–413; Chem. Abs., vol. 29, 1935, p. 2124.

Describes apparatus for following changes of weight continuously by measuring the current required by a solenoid to counteract the displacement of a magnet attached to a silica spring, which is connected to a Pt bucket containing the sample. The material used was pure Fe_2O_3 and Anshan hematite, containing Fe_2O_3 93.89, Fe_3O_4 2.61, SiO_2 2.42 and Al_2O_3 1.08%. The reduction takes place in the stages $Fe_2O_3\rightarrow Fe_3O_4\rightarrow Fe$. The reduction to Fe_3O_4 is rapid at all gas velocities; further reduction increases with increasing gas velocity up to 120 cc. per min. At constant gas velocity, the rate of reduction of Fe_3O_4 increases with the temperature, being rather slow up to 450°. The curves showed no breaks coresponding to FeO, and its absence was proved by X-ray photographs of samples at varying stages of reduction.

Gottlieb, S. *See* abs. 924, 925.

1228. Goubeau, J. [Investigation of the Optical Analysis of Gasolines.] Brennstoff-Chem., vol. 23, 1942, pp. 1–7; Chem. Abs., vol. 36, 1942, p. 3033.

Data obtained by the Raman spectral analysis are discussed. Comparative tables show good checks with analytical results obtained by other methods. Particular stress is placed on the anlysis of Kogasin.

1229. Goutal, E. [Preparation of Synthetic Petroleum by the Andry-Bourgeois and Olivier Process.] Chaleur et ind., vol. 5, 1924, Special No., pp. 90–96; Chem. Abs., vol. 19, 1925, p. 1194.

Process consists essentially in making water gas, hydrogenating catalytically at 230° at atmospheric pressure to produce CH_4, decomposing into C_2H_2 and H_2 in an electric furnace at 2,000°, and hydrogenating the C_2H_2 catalytically at 150°–300° under a pressure of ½ atm. Products having a calorific value of 2,850 cal. are obtained by expenditure of 12,100 cal.; but raw materials having little or no commercial value (wood waste, high-ash coal, etc.) can be utilized. Discusses economic importance of process.

Goutel, F. *See* abs. 2720, 2721.

1230. Graefe, E. [Ceresin From Coke.] Öle, Fette, Wachse, Seife, Kosmetik, vol. 43, No. 13, 1936, pp. 1–4; Jour. Inst. Petrol. Technol., vol. 23, 1936, p. 78A; Chem. Abs., vol. 31, 1937, p. 241.

Discusses production of hydrocarbons by catalytic reduction of CO and CO_2 of water gas. Comparatively lower working temperatures yield wax products of high melting point, called synthetic ceresin. The product melting at 96° is capable of taking up more solvent and remain a paste than natural ceresin, paraffin, montan wax, etc.

1231. ———. [Ceresin From Coke.] Petrol. Ztschr., vol. 32, No. 37, 1936, pp. 5–8; Refiner and Nat. Gasoline Mfr., vol. 16, 1937, pp. 335–337; Chem. Abs., vol. 31, 1937, p. 5137.

Properties of the wax produced in the Fischer benzine synthesis are briefly discussed (*see* abs. 1828). Its high oil-binding properties make it suitable for the preparation of polishes, etc. It may also prove a useful source of fatty acids, into which it can be converted by oxidation.

GRAETZ, A. *See* abs. 410.

GRAF, E. *See* abs. 2339.

GRAFINS, M. A. *See* abs. 3025.

GRAGES, E. *See* abs. 1504.

GRASS, R. C. *See* abs. 1217.

1232. GRASS, R. C., AND STORCH, H. H. Coal-to-Oil Research at Bruceton, Pa. Chem. and Eng. News, vol. 28, No. 9, 1950, pp. 646–648.

Progress report on the conversion of coal to liquid fuels by the 2 basic processes and their variations: The Bergius process of direct hydrogenation of coal and the Fischer-Tropsch process of indirect hydrogenation of coal by way of synthesis gas. Some of the reseach activities that have not been described in the literature are touched upon.

1233. GRAUE, G., AND KOCH, H. W. [Diffusion of Gases in Solids, Studies on Iron Oxide and Iron Aluminum Oxide.] Ber. deut. chem. Gesell., vol. 73, B, 1940, pp. 984–995; Chem. Abs., vol. 35, 1941, p. 3151.

Atomic pores of highly dispersed materials remain accessible by the addition of certain substances. Effect of Al_2O_3 (A) was studied on increasing the accessibility to gases of the inner surface of röntgenographically amorphous Al_2O_3–Fe_2O_3 (AF) catalysts obtained by precipitation at 20°. The porosity was determined by the Hahn built-in radioactive-substance emanation method. On heating (AF) the atomic diffusion pores decrease to nearly zero at 600°; for pure Fe_2O_3 (F) corresponding parts of the curve lie about 100° lower. The density of Fe_2O_3 increases on heat treatement from 3.7 and 3.3 at 250° and 4.9 and 4.4 at 450° to 5.1 and 5.1 above 600° as measured by the emanation and the xylene-20°-pycnometric methods, respectively. Although pure (F) rapidly ages to a maximum density of 5.1 when heated at 450°, the (AF) catalysts age only slowly and still show differences in density as measured by the 2 methods. The absolute rate of diffusion of gases in (AF) as measured by the emanation method is greater than in (F), and increases again at high temperatures, but the Tammann position-exchange temperature is about 820° for the (AF) and only 620° for (F) catalysts. Above 600° for (F) and 700° for (AF) diffusion into the lattice leads to abnormally high values of the density which are not observed by the xylene method. Debye-Scherrer X-ray photographs give the same maximum for both, but the observed intensities of the maximum are greater for (F) than for (AF). It is concluded that (A) is dissolved in the (F) lattice and that its addition in some way hinders the mobility of the lattice constituents until higher temperatures are reached.

1234. GRAUE, G., AND RIEHL, N. [Size of the Pores and Inner Volumes of Amorphous and Crystalline Materials.] Ztschr. anorg. Chem., vol. 233, 1937, pp. 365–375; Chem. Abs., vol. 32, 1938, p. 18.

Specific tests show that gases do not penetrate into catalysts through the large pores alone. Where there is random distribution or where the arrangement of the lattice lacks regularity, the irregular spacing of the atoms allows penetration, even through openings of atomic dimensions.

1235. GRAVES, G. D. Higher Alcohols Formed From Carbon Monoxide and Hydrogen. Ind. Eng. Chem., vol. 23, 1931, pp. 1381–1385; Chem. Abs., vol. 26, 1932, p. 1235.

Several higher alcohols have been identified as by-products of the industrial high-pressure MeOH synthesis: 1–propanol, isobutanol, 2–methyl–1–butanol, 2–methyl–1–pentanol, 2, 4–dimethyl–1–pentanol, 4–methyl–1–hexanol, isopropanol, 3–methyl–2–butanol and 2, 4–dimethyl–3–pentanol. Strong evidence for the presence of the following was obtained: 2, 4–dimethyl–1–hexanol, 4– or 5–methyl–1–heptanol, 3–pentanol, 2–pentanol and 2–methyl–3–pentanol. Acids, esters, ketones, olefins, and tertiary alcohols were absent. The presence of all the products identified can be accounted for by assuming that the mechanism of synthesis is intermolecular dehydration of 2 lower alcohols involving H_2 either from the hydroxylated C atom or the adjacent C atom. H separates most readily from a CH_2 group, more difficultly from a Me group, and not at all from a CH group.

GRAYSON-SMITH, H. *See* abs. 1624.

1236. GREAT BRITAIN COMMITTEE OF IMPERIAL DEFENCE, SUBCOMMITTEE OF OIL FROM COAL. Falmouth Report on the Production of Oil From Coal. H. M. Sta. Office, London, 1938, 71 pp.; Coal Carbonisation, vol. 4, 1938, pp. 46–48.

Committee's report on the Fischer-Tropsch process has little value, as the evidence obtained is conflicting. The general, though indefinite, conclusion to be drawn therefrom is that the capital cost and economics of a Fischer-Tropsch plant would be similar to that of a coal-hydrogenation plant. The committee recommends "the establishment of a plant to work the Fischer process, and designed for the production of not less than 20,000–30,000 tons of primary products per annum." This is the commercially economic size of plant for the operation of this process.

1237. GREAT BRITAIN FUEL RESEARCH BOARD. Lubricating Oil. Fischer Process. Rept. for the Year Ended Mar. 31, 1935, pp. 122–123.

In working on the synthesis of liquid hydrocarbons from mixtures of CO and H_2, products have been obtained that embrace the entire series of paraffins from CH_4 to hard paraffin wax with the related olefins, but contain no fraction corresponding to a lubricating oil. Recently, however, products are reported, the specifications of which are those of excellent lubricants. These are formed by the polymerization with $AlCl_3$ of the fractions that are rich in unsaturated hydrocarbons. Some investigation has been made sufficient to confirm the nature and conditions of the synthesis reaction.

1238. ———. Production of Hydrocarbons From Water Gas by the Fischer Synthesis. Rept. for the Year Ended Mar. 31, 1936, p. 148.

Laboratory-scale apparatus capable of treating 10–15 l. of gas per hr. has been designed and operated. The results fully confirm those of Fischer. The catalyst used is Co promoted with Th supported on kieselguhr. Pelleting the catalyst considerably increases the volume of gas that can be treated in a unit of time in a given volume of catalyst space. Examination of the absorption spectra of the oils produced show these to have a definite though small content of aromatic hydrocarbons; the presence of benzene, toluene, and naphthalene was detected in amounts of from 0.1–1.0%. Small samples of lubricating-oil fractions have been produced from the primary products by treatment with anhydrous $AlCl_3$. On the basis of the experience gained with the laboratory-scale apparatus, a plant of sufficient capacity to give 1 l. of lubricating oil per day will be constructed.

1239. ———. Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Rept. for the Year Ended Mar. 31, 1937, pp. 141–147.

Laboratory investigation on the synthesis of hydrocarbons from CO and H_2 has been directed mainly to determine the influence of the % of ThO_2 promoter on the activity of the Co catalyst, and the effect on the yield of hydrocarbons of changing the ratio CO : H_2. No conclusions have been reached. As to the mechanism of the synthesis reaction, the evidence points toward the Fischer carbide theory, although an alternative theory is postulated that the CO molecules are first linked to the catalyst surface, forming a bond similar to that existing in a Co carbonyl molecule, except that the metal atom is not detached from the lattice. The H_2 absorbed on adjacent Co atoms may then react with the absorbed CO, attacking either the O_2 or the C atom. In the latter case, HCHO would be formed as an intermediate product. Neither of the above hypotheses explains how the methylene or other radicals first formed link up to give the long hydrocarbon chains. A plant, large enough to convert 100–150 cu. ft. of a mixture of H_2 and CO per hr. into hydrocarbons has been designed and constructed. A flow diagram of the plant is shown. Catalyst cooling is accomplished by circulating hot water under pressure through horizontal tubes in the catalyst bed. Details of catalyst preparation are presented, and the importance of washing the precipitated catalyst with boiling H_2O is emphasized. With the unwashed catalyst no contraction took place, even at a temperature of 238°, whereas with the washed catalyst a contraction of 65% at 198° took place and was maintained for 24 hr. At an equivalent gas rate per gm. of catalyst, the catalyst that had been washed and electrodialyzed brought about a contraction of 71% at 193°. Some difficulty was found in transferring the catalyst preparation from the laboratory to the larger scale, the causative variables have not been determined.

1240. ———. Production of Synthesis Gas. Rept. for the Year Ended March 1938. H. M. Sta. Office, London, pp. 134–135.

In connection with water-gas experiments, a process has been adapted for producing synthesis gas for the Fischer-Tropsch process by combining the Lane process of H_2 production with the normal water-gas process. The Lane process consists of the alternate reduction and oxidation at 700°–800° C. of calcined spathic Fe ore, the reduction being effected by water gas and the oxidation with production of H_2 by steam. The Research Board process involves removing the checker brickwork from the tar cracking chamber and its replacement by spathic Fe ore. The temperature of the ore is raised to 700°–800° by the flow gases and is then reduced by passing through it the water gas produced during the up-run. The spent gas from this reduction (calorific value 200 B. t. u. per cu. ft.) is collected in a separate gas holder. H_2 is produced by passing the back-run steam through the reduced ore, a part of the steam being decomposed by the reduced Fe ore with the production of H_2 and the excess steam passed to the generator containing coke, where normal water gas is made. The finished gas contains 32.3% of CO and 61.9% of H_2.

1241. ———. Synthesis of Hydrocarbons and the Production of Lubricating Oils. Rept. for the Year Ended March 1938. H. M. Sta. Office, London, pp. 186–206.

Investigations have extended from a study of the mechanism of the synthesis, through laboratory-scale and semi-technical-scale plant work, to an examination of the quality of the products under practical conditions. Investigation of the mechanism leads to the conclusions that carbide formation proceeds much more rapidly when CO reacts at 200° with an active Fischer catalyst than with ordinary reduced Co; that the carbide formed reacts very readily with H_2 to give a gas consisting mainly of CH_4 and a small % of higher hydrocarbons; that the rate of reaction of the carbide with H_2 is very much greater than its rate of formation from CO and the catalyst. By studying the *o–p*–H_2 conversion on the catalyst during the synthesis reaction, it is found in general that, if the conversion is being catalyzed by a metal, adsorbed H atoms are present on the metal surface; and, if on the other hand, conditions are such that no absorbed H atoms can be formed on the surface, the metal will not catalyze the *o–p* conversion. The results of experiments show that when the product is higher hydrocarbons, no H atoms are detectable on the surface, but when the product is CH_4, H atoms are there. Thus it seems reasonable to conclude that if the chemisorbed CO is attacked by adsorbed H atoms, the product will be CH_4, but attack by molecular H_2 leads ultimately to higher hydrocarbons. Previous difficulties in catalyst preparation have been largely removed and a satisfactory composition has been found in Co : ThO_2 : kieselguhr=100 : 18 : 100. Before the semi-technical-scale plant runs, described in detail, the catalysts was reduced in H_2 at 350°, compared with the operating synthesis temperature of 180°–230°. The highest yield of recovered oil product was 77.0 gm. per N m.^{3} of synthesis gas (exclusive of lighter constituents). This yield has later been improved to 90–100 gm. per m.^{3} The crude product consists almost entirely of straight-chain paraffins and olefins, from the lightest member of the series up to wax having a melting point above 100°. Appropriate fractions may be used as motor fuel and diesel oil, the former of very low antiknock value (30 by the Cooperative Fuel Research Committee method), the latter with a high cetene number (93). Important possibilities of the process lie in the polymerization with $AlCl_3$ of the unsaturated constituents of the product to form lubricating oil, considerable details of which are presented. Some experiments have been carried out on the oxidation of the wax for the production of fatty acids, and it has been shown possible to produce a soap by this means. The procedure is to oxidize the wax at 100°–130° with 0.25–0.5% Mn resinate as catalyst. The only point in which the synthetic lubricating oils fall short of high-grade natural products is that they failed to pass the test with respect to increase of viscosity on oxidation associated with formation of acidic and saponifiable substances.

1242. ———. Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Rept. for the year Ended March 1939. H. M. Sta. Office, London, pp. 151–176.

Continuation of the investigations begun in 1937–38 gives further account of the operation of the plant and of the yields obtained during a run lasting more than 2 mo. An important aspect of the process is the possibility of using certain fractions of the crude product for the preparation of lubricating oils. During the most favorable stage of the run, the yield of recovered liquid hydrocarbons was over 90 gm. per N m.^{3} of synthesis gas and, in addition, about 10 gm. per m.^{3} of easily condensible hydrocarbons and 3 gm. per m.^{3} of hard wax. The rate of input of synthesis gas was standardized at 120 cu. ft. per hr. The normal synthesis was started at 186° and progressively raised to 215° as the activity of the catalyst diminished. It was found necessary, at least at the end of each 24-hr. period and sometimes oftener, to revivify the catalyst by passing H_2 over it for 1 or 2 hr., after which a spurt in the activity occurred accompanied by the production of excessive amounts of CO_2. To obtain the best results, a special "running-in" technique of the catalyst had to be observed. Further data regarding the synthesis mechanism indicate that carbide is not formed on the catalyst in the usual way $2Co+CO \rightarrow Co_2C+CO_2$ but rather by $2Co+CO+H_2 \rightarrow Co_2C+H_2O$. These conclusions are confirmed and put on a quantitative basis by measuring the rates of the various reactions at a series of temperatures and so obtaining the corresponding energies of activation; that of (1) is 18,000 cal., that of (2) 9,500 cal., and that of the reduction of carbide $Co_2C+2H_2 \rightarrow 2Co+CH_4$, 11,500 cal. The results indicate that reaction (1) wil not occur during the Fischer synthesis, and that the formation of carbide by reaction

(2) will occur, followed by its reduction to CH_2 groups. Previous work on the *o–p*–H_2 conversion has proved that in the presence of large amounts of chemisorbed H_2 these CH_2 groups are reduced further to give CH_4; when, however, the amounts of chemisorbed H_2 is small, they polymerize and give higher hydrocarbons. It is reasonable to suppose that the larger numbers of CH_2 groups produced on the surface during the synthesis are equivalent to a macro-molecule from which fragments can be broken off to form the Fischer products. If so, cracking of paraffin hydrocarbons should occur on the catalyst at 200° by interaction of the paraffin hydrocarbon with chemisorbed H_2, and hence in the Fischer synthesis the products actually obtained are hydrogenation-cracking products of the macro-molecules of CH_2 groups, caused by the presence of quite small amounts of chemisorbed H_2. In the presence of larger amounts the hydrogenation-cracking is carried so far that CH_4 only is produced.

1243. ———. Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Summary Report for the Period 1940–45, based on information from Dr. C. C. Hall, 1947, 12 pp.

Work is summarized in 2 parts: Study of the synthesis process, particularly the production of lubricating oils and the working-up of the primary products. The apparatus was the same as previously described, except that the oil jacket used as the heating and temperature-regulating means was replaced by a vertical steel tube embedded in an electrically heated Al block. The most active catalyst at the reaction temperature of 185° and at atmospheric pressure, was found to be Co : ThO_2 : MgO : kieselguhr= 100 : 5–6 : 2–8 : 200–300, reduced by H_2 at a high velocity (5,000–6,000 vol. per vol. of catalyst per hr.) for 2 hr. at 380°–420° C. It could be dewaxed by passing H_2 at 185°–200° and entirely regenerated by repeating the original high-temperature reduction in H_2. It was found that the initial life (the period up to the first H_2 dewaxing treatment) of this catalyst was appreciably increased by operating at a temp. of 185° from the start, instead of raising it from 175° to 185° gradually. The maximum converter life (the period between the original reduction and the re-reduction) is obtained when the H_2 dewaxing treatment is carried out at short intervals (7–10 days) and the temperature raised as slowly as possible. The conditions necessary for maximum total life (the period up to re-manufacture) are not fully known, although evidence has been obtained that restricting the maximum synthesis temperature to 195° during each converter life is beneficial. One of the most important factors affecting the performance of the Co–ThO_2–MgO catalyst is the nature of the kieselguhr used as carrier. The best one yet tested was of Portuguese origin. It gave a robust catalyst of high activity and long life and, as a result of the high density, a high space-time yield. It was thought possible to avert deterioration of the catalyst by wax deposition by maintaining a higher partial pressure of H_2 during the synthesis, but such improvement was nullified by an undesirable increase in CH_4 formation. Neither did a decrease in the reaction temperature help the situation since any reduction in CH_4 by this means was offset by the formation of wax. Dilution of the synthesis gas with N_2 at a constant gas rate of 1 l. $CO+2H_2$ per gm. Co per hr. causes a marked fall in total conversion and a serious reduction in liquid hydrocarbons. When CH_4 is used as a diluent it enters into the reaction, giving a 10–20% higher yield of liquid hydrocarbons per m.^{3} of CO and H_2 than when N_2 is used and at the same time a greatly enhanced yield of C_3 and C_4 hydrocarbons. It has not yet been established whether this reaction persists or is merely confined to the initial phase of high catalyst activity. Use of gas rates 1½ times and 2 times normal causes a sharp fall in conversion and, initially, a more rapid deterioration, which later, however, becomes no greater and may be even less than at normal rate. Catalysts with a high Co density (12 or more gm. Co per 100 ml.), which operate satisfactorily at atmospheric pressure with a high space-time yield, have been found unsatisfactory for synthesis at medium pressure. Excessive CH_4 production occurs and lower yields of liquid and solid hydrocarbons. When water gas is used instead of normal synthesis gas, however, excessive formation of CH_4 is suppressed, and yields of liquid and solid hydrocarbons as high as those for catalysts of normal density (7–9 gm. Co per 100 ml.) are obtained. Only slight work has been performed on Fe catalysts and of those tested, none has given the consistently good yields (130–140 gm. per *N* m.^{3}) obtainable with Co catalysts at 10 atm. pressure. Addition of C_2H_2 to the synthesis gas was tried to determine if branched-chain hydrocarbons might be formed. An increase in the octane number of the gasoline fraction from 30 to 78 was obtained but it was found that this increase was due to the olefins and aromatic hydrocarbons formed by the reaction between C_2H_2 and H_2 independently of the reaction between CO and H_2. The formation of rubberlike polymers also caused rapid deterioration of the catalyst. The carbide mechanism of the Fischer–Tropsch process is supported and further extended through experimental studies. The production of lubricating oils by polymerization of the primary, olefin-containing Fischer–Tropsch products has received further detailed study with emphasis on the use of water gas rather than synthesis gas as the raw material. An extensive study has also been made, and the results have been summarized of the production of fatty acids for the preparation of soap or edible fats by the controlled oxidation of Fischer–Tropsch wax of initial b. p. 300° and average molecular weight 315 prepared in the semi-technical-scale plant.

1243a. ———. Oils and Chemicals From Coal. Report of the Fuel Research Board for 1949–50; Chem. Age, vol. 66, 1952, pp. 371–374.

Study of the Fischer–Tropsch synthesis had been continued. The work based on Co catalysts was concluded as Fe catalysts were found to be cheaper and more flexible in operation in the fluidized and liquid-phase processes. Operation of a 30–50 gal. daily capacity pilot plant was begun. Work was carried out with Fe catalysts at 20 atm. and 300°–320° temperature. Formation of CO_2 was suppressed and the linear gas velocity necessary for fluidization was maintained by recirculation of 3–10 vol. residual gas with each volume of fresh synthesis gas. Yields of C_5 and higher hydrocarbons increased at the expense of the C_2–H_4 hydrocarbons. However, formation of free C and of CH_4 was increased and the degree of unsaturation of the products was reduced. The fused NH_3–synthesis catalyst gave lower yields of liquid hydrocarbons and H_2O–soluble compounds containing O and higher yields of CH_4 than the sintered mill-scale catalyst. Best operating results were obtained when using a mill-scale catalyst diluted and expanded by C formation so as to contain about 200 gm. Fe per liter as compared with 1,800 gm. Fe per liter for freshly reduced catalyst. Depth of the slurry through which the synthesis gas passed was not a significant factor. Proportion of gas that reacted and the yield of products appeared to be controlled by the gas throughput per volume of slurry rather than that per volume of catalyst. Best performance was obtained with a slurry containing about 300 gm. reduced catalyst per liter. The maximum gas rate consistent with satisfactory conversion was about 500 vol. fresh gas per vol. slurry per hr. Effect of reaction conditions on the proportion of alcohols in the products was investigated. Temperature and pressure had the greater influence, the proportion of alcohols increasing with fall of reaction temperature and increase in pressure. An increase in the rate of gas flow, and a decrease in the ratio H_2 : CO in the gas both favored production of alcohols.

1244. ———. Synthesis of Methane. 5th Annual Rept., 1943–44, pp. 13–25; Gas Abs., vol. 1, No. 7, 1945, p. 10.

Problem of the synthesis of CH_4 from CO and H_2 by means of promoted Ni catalysts at 350°–800° C. and at pressures 1–50 atm. has been investigated separately by the Gas Research Board Laboratories and the Fuel Research Station in Britain. Both laboratories have studied methods to prevent (*a*) the loss of activity of the catalyst due to overheating, which causes a diminution of active surface (sintering) and (*b*) deposition of C at higher temperatures. Their suggested means of overcoming these difficulties are in fairly close agreement: (1) Catalysts prepared by the precipitation of nitrates with alkali as carbonate in the presence of kieselguhr support, followed by a very thorough washing, are more resistant to heat treatment and give a much lower C deposition than those obtained by impregnation, that is, ignition of the absorbed nitrates on the support. (2) Overheating, or sintering, as well as the rate of C deposition, depends on the effective removal of the exothermic heat of reaction and increases with increasing working temperatures. At 700° C. the life of the catalyst becomes relatively short. However, at 800° C. an extremely long life was observed in spite of sintering, probably because at such high temperature the reaction is no longer dependent upon specially active atoms in the catalyst. (3) The rate of C deposition depends upon the nature of the support. Catalysts of identical composition supported on kieselguhr from 1 source gave 10 times more C deposition than those on kieselguhr from another source. (4) C deposition decreases as the size of the catalyst granules increases. Heat dissipation is also favored by the use of a narrow catalyst space surrounded by a jacket containing a high-boiling liquid. (5) The admixture of steam with the process gas decreases C deposition, and 15% steam (by volume) entirely prevents it. (6) The higher the H_2: CO ratio the less the tendency to deposition of C. The amount of steam required by gases of various H_2: CO ratio in preventing C deposition is shown by curves for various temperatures 350°–600° C.

1245. ———. Synthesis of Methane. 6th Annual Rept., 1944–45, pp. 18–32.

Since the 5th report (*see* abs. 1244) a medium-scale plant has been designed to allow purification from S compounds of the synthesis gas, the modification of the proportions of H_2 and CO in the gas, and the division of the gas into streams for evaluation of a number of variables including pressure, each stream carrying about 250 cu. ft. of gas per hr. Methods were recorded in the 5th report for controlling the heat of reaction by (1) recirculation of gas, (2) the use of rod-shaped catalysts over which streamline conditions of flow were maintained, so that the rate of diffusion of gas to the surface of the catalyst controlled the rate of reaction by giving a natural distribution over a wide surface, and (3) the use of forced distribution by means of a perforated feed pipe extending over a length of catalyst surface. Using methods (2) and (3), life periods of over 2,000 hr. were maintained at gas velocities of 2,000 vol. per vol. of catalyst per hr., and with method (3) it was possible to use a synthesis gas as low as 1.0 in H_2: CO ratio, and to avoid C deposition for 2.700 hr. Some study of the reactions involved in C deposition were made. Variations have been made with some success in the composition of the standard Ni catalyst, with the object of preventing deposition of C. Further studies have also been made of the increases in temperature over the catalyst surface and of the connection between this temperature and loss of activity due to sintering. Little success has been obtained in employing MoS as a CH_4-forming catalyst resistant to poisoning by S, but the potentialities are so great that the work will be continued. Experimental details are given in tabular and graphic form on the effect of additions to the catalyst of S, Mn, and Al on C deposition; S up to 0.2% of the Ni and Al in excess were favorable in their effect. Mn favored C deposition. The S-containing catalyst resists sintering less effectively than does the Al-containing catalyst. Other experiments studied the influence of space velocity, control temperature, and size of catalyst granule upon the maximum temperature developed in a column of granulated catalyst at atmospheric pressure with dissipation of reaction heat. The mechanism of C deposition on the Ni catalyst involves the formation of NiC by the reaction between CO and Ni at 200° and the subsequent breakdown of this into Ni and C. The Fuel Research Station has studied the effect of the carrier on C deposition on catalysts of Ni–ThO_2–MgO–kieselguhr and has concluded that a kieselguhr with low specific surface area promotes the most rapid C deposition. Calcination of the kieselguhr is best carried out at 700°–800°. It was also found that the effect of heating the catalyst in H_2 was to decrease the activity for CH_4 synthesis and to increase the tendency to deposit C. The addition of small proportions of P and S reduces its tendency to C deposition but increases the rate of deterioration; the addition of 0.2% S as $NiSO_4$ reduced the rate of C deposition with process gas H_2: CO=1.5 : 1 from 0.462% to 0.157%, but reduced the active life with gas of H_2: CO=3.0 : 1 and space velocity 3,700 vol. per vol. per hr. from 1,700–910 hr.

1246. ———. Synthesis of Methane. 7th Annual Rept., Commun. 24, November 1946, pp. 20–38; Gas Times, vol. 54, Feb. 27, 1948, p. 295; Fuel Abs., No. 3536, June 1948.

Research work has been continued by both the Gas Research Board and the Fuel Research Board on the catalytic synthesis of CH_4 as a means of gas making or gas enrichment, and progress is reported in the study of the reactions involved in the development of simpler and more effective catalysts and in the methods of purification of the synthesis gas from organic S compounds. The study of the mechanism of the reactions leading to the deposition of C on catalysts has been continued, but so far none of the findings has been applicable to the general problem of controlling the CH_4 synthesis reaction on an increased scale. Laboratory-tested variations of known methods of control of catalyst temperatures will be studied, including (1) recirculation of gas, (2) the use of rod-shaped catalysts over which streamlined conditions of flow are maintained so that the rate of diffusion of gas to the surface of the catalyst controls the rate of reaction by natural distribution, and (3) the use of perforated inlet pipe extending along or through the catalyst column and providing mechanically controlled distribution. Some success has been found in the use of an annular layer of granulated catalyst with which the reaction gases make contact progressively along its length through perforations in an inner tube. At a rate of 120 cu. ft. of synthesis gas per hr., the extent of C deposition has been greatly reduced. Modified Ni–Mg catalysts have been developed which are active enough to be operative at temperatures down to 186°, not only with synthesis gas but also with town gas. Studies have also been made of the effects of the conditions of preparation of the catalysts, and of their activity at stages during progressive poisoning by S.

1247. ———. Report of the Director for 1947. Commun. 37, 1948, 55 pp.; British Abs., 1948, B, I, p. 370.

Some of the subjects dealt with are: (*a*) Direct hydrogenation of coal. Difficulties in temperature control and in dissipating the heat of reaction in a static bed of coal have turned attention to the hydrogenation of fluidized coal, for which a high-pressure apparatus has been constructed. (*b*) Synthesis of CH_4. The pilot plant with temperature control by circulation of the gases has operated satisfactorily, the catalyst keeping its full activity for 3,500 hr. at 20 atm. A life test is to be made at 1 atm. While the surface area of the $Ni–Al_2O_3$ catalysts is not a measure of their activity, its retention without diminution when heated is an indication that activity will be maintained in use. (*c*) Water-gas process. (*d*) Removal of organic S compounds from gas. (*e*) Removal of H_2S by Fe_2O_3.

1248. Great Britain Hydrocarbon Oil Duties Committee (Sir Amos L. Ayre, Chairman). Report of Hydrocarbon Oils. Coke Smokeless-Fuel Age, vol. 7, 1945, pp. 88–90; Chem. Trade Jour., vol. 116, 1945, pp. 423–426; Chem. Age, vol. 52, 1945, pp. 343–345; Petrol. Times, vol. 49, 1945, pp. 304–309.

Report, with comments indicating the importance of developing chemical manufactures based on coal by products. It is recommended by the committee that imported hydrocarbon oil used for chemical synthesis should be free of duty and for indigenous oil similarly used, allowances should be paid equal to the respective duties. An interesting feature of the Fischer-Tropsch process is that the products are aliphatic, not aromatic, in character and thus resemble petroleum rather than coal oils produced by other processes. Many of the more important chemicals which can be produced from petroleum could therefore be derived with equal and, in some cases, greater facility from the primary products of hydrocarbon synthesis.

1249. Great Britain: Northern Industrial Group. Coal Processing Industries Panel (H. L. Riley, chairman). Coal-Processing Industries Report. Chemicals From Coal in the North. Chem. Age, vol. 53, 1945, pp. 565–568.

Objectives to be considered are development of the tar-distillation industry and extraction of C_2H_4 from coke-oven gas. The statment is made that the north-east 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.

1250. Grebel, A. [Practical Substitute Fuels: Particularly Synthetic Fuels.] Chaleur et ind., vol. 6, 1925, pp. 273–282; Chem. Abs., vol. 19, 1925, p. 3007.

From a detailed discussion of the problem, Grebel concludes that a successful gasoline substitute should fulfill at least the following conditions: O less than 25%, H 7–16%, calorific value over 7,000 cal. per l., thermal potential (cal. per $m.^3$ of perfect explosive mixture) over 750, flash point as little below 20° as possible, price per 1,000 cal. between that of petroleum and of gasoline.

1251. ———. [Coal as a Source of Liquid Fuels.] Mat. grasses, vol. 19, 1927, pp. 7958–7961, 7984–7987, 9011–9013; Chem. Abs., vol. 22, 1928, p. 1226.

Address.

1252. ———. [Processes for the Manufacture of Liquid Hydrocarbons as Fuels for Explosion and Internal-Combustion Engines, Starting From Mineral Fuels.] Chaleur et ind., vol. 8, 1927, pp. 324–332; Chem. Abs., vol. 21, 1927, p. 2779.

Critical review of recent processes, particularly the Bergius, Fischer-Tropsch and Prudhomme-Houdry.

1253. Greenfield, G. J. Coal Gas as a Raw Material. Coke Smokeless-Fuel Age, vol. 2, 1940, pp. 201–202, 204; Chem. Abs., vol. 35, 1941, p. 1206.

Typical coke-oven gases are classified according to analysis: Valueless: CO_2 4, N_2 5, H_2S+HCN 1; low-calorific-value gases: H_2 54, CO 4; high calorific-value gases: CH_4 29, illuminants 3%. A possible treatment is to pass this gas with steam over heated catalysts, converting the CH_4 into CO and H_2. This resulting mixture opens up a vast field to the synthetic chemical industry.

Greenfield, H. *See* abs. 3655, 3655b.

1254. Greenwood, H. D. Technical Developments During 1936 in the Gas and Allied Industries. Fuel Econ. Rev., 1937, pp. 49–54; British Chem. Abs., 1938, B, p. 12.

Carbonization of cannel coal, the Fischer-Tropsch process, and the removal of S compounds from town gas are discussed.

1255. Gregg, S. J., and Jacobs, J. Examination of the Adsorption Theory of Brunauer, Emmett, and Teller, and Brunauer, Deming, Deming, and Teller. Trans. Faraday Soc., vol. 44, 1948, pp. 574–588; Chem Abs., vol. 43, 1949, p. 2065.

Brunauer-Emmett-Teller and Brunauer-Deming-Deming-Teller theories have been examined, and the following points are discussed: The heat of adsorption E_1 calculated via the parameter *c* of the theory, is shown to be compatible with thermo-dynamic requirements as expressed in the Clausius-Clapeyron equation, but the latter are equally compatible with a value E_1+RT in C, where C=any constant. E_1 shows a moderate qualitative correspondence with the calorimetric or isosteric value, but close quantitative agreement is lacking. The relationship, which the theory implies between I_L and I_x, the integration constants of the vapor equation and the adsorption isostere, respectively, is not found to hold in practice. Arguments are adduced against the assumption made by the theory that the evaporation-condensation conditions of the adsorbed multilayer differ inappreciably from those of the bulk liquid. The implicit assumption that the adsorption isotherms above and below the critical temperature of the adsorbate are markedly different is shown to be improbable. The values of the monolayer capacity derived from the theory and from the "phase-change" method of Gregg and Maggs are compared; only for isotherms of types I and II of the BDDT classification is agreement to be found. According to the phase-change method, the adsorption isotherm cannot invariably be represented by a single equation as assumed by the BET-BDDT theory; where phase changes occur, the isotherm is split up into separate parts each following its own equation. The BET-BDDT theory does not account for hysteresis, but the phase-change conception includes it as a natural consequence.

1256. Griffin, C. W. Adsorption of Hydrogen by Supported Nickel Poisoned With Carbon Monoxide. Jour. Am. Chem. Soc., vol. 59, 1937, pp. 2431–2434; Chem. Abs. vol. 32, 1938, p. 1158.

Adsorption was measured at 0° for H_2 on a supported Ni catalyst poisoned with CO. A small quantity of poison causes an increase of H_2 adsorption at all pressures up to 1 atm. A large amount of poison gives a slight low-pressure increase and a high-pressure decrease of adsorption. Larger amounts of poison decrease the rate of adsorption.

1257. ———. Sorption of Hydrogen by Poisoned Copper. Temperature Variation Experiments. Jour. Am. Chem. Soc., vol. 67, 1945, pp. 62–64; Chem. Abs., vol. 39, 1945, p. 1342.

The sorption of H_2 with temperature variation on pure massive Cu was determined and compared with that of H_2 on the same Cu poisoned with a small quantity of CO. The effect of the poison is to prevent largely solution of H_2 in Cu.

1258. Griffith, R. H. Catalytic Removal of Sulfur Compounds. Inst. Gas Eng., Copyright Pub. 175/64, 1937, pp. 45–64; Gas Jour., vol. 220, 1937, pp. 475–476, 479–485, 667; Gas World, vol. 107, 1937, pp. 379–383, 471–476, 563; Chem. Abs., vol. 32, 1938, p. 6438.

An active $Ni(OH)_2$ catalyst is deposited on porous china clay by soaking in a boiling solution of $NiCl_2$, drying, plunging the pellets into excess alkali, washing, and activating with coal gas at 350° for 2 hr. Purified coal gas was passed through the catalyst bed at about 1,500 vol. per hr. per unit vol. of catalyst space at an inlet temperature 160°–180°. In an experimental run of 40 weeks, 10,000,000 cu. ft. of gas were treated without renewal or alteration of the catalyst. CS_2 was converted to CO_2 and SO_2 with small porportions of SO_3. If temperature rose too high, a back reaction occurred, and H_2S was produced by hydrogenation of SO_2. Temperature can be controlled by adjustment of O_2 in gas; the normal amount is 0.6–0.7%. Combustion of H_2 and complete elimination of O_2 increase calorific value, permitting extraction of more benzene. Heat requirements are met by exchange between outgoing and incoming gas. Gas treated by the catalytic process and then by active charcoal for recovery of benzene should contain less than 1 gr. S per 100 cu. ft. of gas, no O_2, no NO, and a considerably lowered % of diolefin hydrocarbons. It should be free from formation of gummy deposits and produce only traces of SO_2 on combustion.

1259. ———. Geometrical Factor in Catalysis. Advances in Catalysis. Academic Press, Inc., New York, 1948, vol. I, pp. 91–114.

Reaction kinetics and mechanism of catalysis are studied from the viewpoint of 2-point adsorption on an active catalyst surface. The reactions of unsaturated organic molecules and of C_2H_2 are discussed. The synthesis of hydrocarbons from CO, and related reactions, are argued, and evidence is brought forward to support the chain-growth hypothesis.

———. *See* abs. 1465.

1260. Griguard, V., DuPont, G., and Locquin, R. Traité de chimie organique. Maison & Cie, Paris, 1937, vol. 5, p. 826.

Discusses MeOH synthesis.

1261. Grimme, W. [Recovery of Liquefied Gases From Coke Ovens, Synthesis and Other Gases.] Ztschr. Ver. deut. Ing. Beih. Verfahrenstech., 1940, pp. 12–16; British Chem. Abs., 1941, B, p. 271.

Light hydrocarbons in coke-oven gas, hydrocarbon-synthesis waste gases, etc., owing to their low concentration, are usually recovered by means of active C. The technique is described and details are given of the working of an active-C plant at a Fischer-Tropsch hydrocarbon-synthesis works.

1262. ———. [Gasoline Products by Direct Synthesis. German Developments in the Fischer-Tropsch Process.] Oel u. Kohle u. Brennstoff-Chem., June 1, 1944; Chem. Trade Jour., vol. 117, 1945, pp. 289–290.

Recovery of the lower-boiling products produced in the Fischer-Tropsch process is discussed. The activated C process is employed. The Fischer-Tropsch feed gas generally contains 15–20% of inert constituents such as CH_4, CO_2 and N_2. From such a gas about ⅓ leaves the catalyst chamber in gaseous form, the hydrocarbons in this exit-gas mixture containing 40–50% of the total hydrocarbons produced in the conversion. Even after cooling, it still contains 200 gm. of gasoline and gas oil per $m.^3$ The activated C, arranged in a tower, has a selective adsorptive action on the gas constituents, the gasoline and gas oil being taken up first. The lower portions of the C become saturated first with gasoline, this gradually displacing upward the lighter hydrocarbons and other products until, at the end of the operation, the C has adsorbed about 5% of its weight of gasoline, which is recovered by steaming. The operation is effected on a large scale in groups of 4 adsorbing columns, 1 of these being cut out automatically in series for regeneration. The lower hydrocarbons recovered may be used for the synthesis of high-octane fuels.

1263. ———. [Fischer-Tropsch Synthesis.] Bergbau Archiv, vol. 9, 1949, pp. 114–121; Coke and Gas, 1949, p. 331.

Reviews process.

Grimnes, F. B. *See* abs. 3108.

1264. Grinevich, V. M. [Carbon Catalyst for Carbon Monoxide Conversion.] Jour. Appl. Chem. (U. S. S. R.), vol. 13, 1940, pp. 831–840 (in French, p. 840); Chem. Zentralb., 1941, I, p. 1209; Chem. Abs., vol. 35, 1941, p. 2286.

Activity of catalysts prepared by impregnating charcoal with K_2S, K_2CO_3, and calcining in the absence of $NH_3–CO$ or CO_2 was low. The catalysts prepared by impregnation of activated fir charcoal with KCNS, or better with K_2S, K_2CO_3, or K_2SiO_3, and calcining in an $NH_3–CO$ or CO_2 stream were nearly as active as the Fe–Mg catalyst. Removal of K from the C catalyst virtually destroyed its activity. Therefore, the action of C catalysts is due to the presence of K compounds distributed on the surface of the carrier (active C). The flash point of C catalysts decreased with an increase in their activity. The presence of Pt in the C catalyst containing K considerably increased its activity. All experiments were carried out at 400° and 500° at a volume velocity of 100 and 600 and steam : gas ratio=3.

1265. ———. Selection of New Raw Materials for Ammonia Catalyst. Jour. Appl. Chem. (U. S. S. R.), vol. 18, 1945, pp. 313–321 (English summary); Chem. Abs. vol. 40, 1946, p. 3576.

Study of Vysokogorsk, Magnitogorsk, and Pokrovsk ores, after magnetic separation from SiO_2, showed the possibility of preparation of an NH_3 catalyst, since the presence of SiO_2 up to 2% does not show a negative effect on the catalyst activity, provided that enough K_2O is present. This effect is explained by separation of much SiO_2 with K_2O in the process of catalyst formation, with consequent formation of essentially pure magnetite crystals. The ore is subjected to double magnetic separation and alkaline fusion and followed by a double separation to yield 23% of finished product. The catalyst can be regenerated by oxidation of KNO_3.

1266. ———. [Zinc-Chrome Catalyst for Methanol Synthesis.] Jour. Appl. Chem. (U. S. S. R.), vol. 18, 1945, pp. 90–96; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 580, 1946; Chem. Abs., vol. 39, 1945, p. 5247.

It was shown that substitution of Cr_2O_3 by CrO_3 in ZnO–Cr oxide catalysts increases catalyst efficiency by 40% in MeOH synthesis. Catalysts 8 $ZnO \cdot 3CrO_3$ and 2 $ZnO \cdot CrO_3$ have the same activity. Increase of Cr to the limit of $ZnO \cdot CrO_3$ lowers the efficiency by 60%. Compression of the catalyst, after a brief working period, improves its efficiency and the mechanical strength.

1267. Grinevich, V. M. and Klapchuk, S. V. [Utilization of the Krivoi-Rog Hematite as a Raw Material for the Ammonia Catalyst.] Jour. Appl. Chem. (U. S. S. R.), vol. 10, 1937, pp. 1868–1870; Chem. Abs., vol. 32, 1938, p. 2298.

Hematite described contains Fe_2O_3 96.70, FeO 0.53, Al_2O_3 0.90, Mn_3O_4 traces, SiO_2 1.60. CaO 0.09. MgO 0.05, S (sulfide) 0.004, S (sulfate) 0.02, and P_2O_5 0.04%. The preparation of catalyst is schematically described. 3 refs.

1268. Griswold, J., and Buford, C. B. Separation of Synthesis Mixtures. Vapor-Liquid Equilibria of Acetone–Methanol-Water. Ind. Eng. Chem., vol. 41, No. 10, 1949, pp. 2347–2351; Chem. Abs., vol. 44, 1950, p. 1788.

Acetone and MeOH are major components of the water product obtained from hydrocarbon synthesis by the Fischer-Tropsch-type process. Vapor-liquid equilibria of the binaries and the ternary are needed in fractionation calculations for separation and recovery of the organic compounds. This ternary and the 3 binary boundary systems were studied completely at 760 mm. Hg pressure. Tabular and graphic data are presented for: $d^{25}{}_4$, $n^{25}{}_D$, boiling point, and vapor-liquid equilibria for all of the systems and actvity coefficients for the 3 binaries only. No ternary azeotropes were found.

1269. Griswold, J., Chu, P. L., and Winsauer, W. O. Separation of Synthesis Mixtures. Phase Equilibria in Ethyl Alcohol–Ethyl Acetate–Water System. Ind. Eng. Chem., vol. 41. No. 10. 1949, pp. 2352–2358; Chem. Abs., vol. 44, 1950, p. 1788.

Above compounds occur in the water product of Fischer-Tropsch type hydrocarbon synthesis processes and in the manufacture of ethyl acetate by esterification. Vapor-liquid equilibria are reported for the AcOEt–EtOH and AcOEt–H_2O binaries as well as for the ternary system. In additon $d^{25}{}_4$ and boiling point (760 mm. Hg) are given. The 2-phase liquid region is explored for the AcOEt–H_2O binary and for the ternary with tie-lines and isothermal boundaries reported. No well-defined ternary azeotrope was found, but a low-boiling zone at 70.3° covering a sizable range in ternary composition was reported along the ester-rich side of the 2-phase liquid region.

Grodde, K. H. *See* abs. 1270.

Groh, E. *See* abs. 3101, 3102.

Groll, E. *See* abs. 1457.

Groll, H. *See* abs.1453.

Gross, —. *See* abs. 1504.

1270. Gross, H., and Grodde, K. H. [Structure of Solid Hydrocarbons as Basis for Classification.] Oel u. Kohle, Erdoel, Teer, vol. 38, 1942, pp. 419–431; Chem. Abs. vol. 37, 1943, p. 5693.

This study of the physical constants of the solid-paraffin hydrocarbons shows that, for a given moleuclar weight, branching of the chain causes lowering of the solidification point, and that presence of rings causes, in addition, an increase in density. In this way a "ring val." (indicating presence of ring paraffins) and an "asymmetry val." (indicating branching of the chains) can be deduced. Heterogeneous mixtures of solid hydrocarbons were examined by separating them acording to molecular weight by fractional distillation and according to their asymmetry by fractional crystallization from solutions in $(CH_2Cl)_2$. Of the products examined, the Fischer-Tropsch synthesis product was a mixture of normal and isoparaffins, that is, of aliphatic nature, while the solid hydrocarbons from petroleum and brown-coal tars contained varying quantities of ring paraffins with different numbers of rings per molecule. The result suggests a classification of solid hydrocarbons on the basis of their composition, solidification points, and ceresin character.

1271. Gross, H. W. [Production of Detoxified City Gas by Pressure Gasification and Synthesis With Iron Catalysts.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 11; No. 5, 1950, pp. 218–222; Chem. Abs., vol. 40, 1950, p. 7513.

Abstract of paper presented at the 1949 meeting of the Deutsche Gesellschaft Mineraloelwissenschaft u. Kohlechemie. Previous processes for the detoxification of city gas, such as the conversion of CO with steam to H_2 and CO_2 or the washing out of CO with Cu salts, have only occassionally been used since they, in general, raise the cost of the gas too greatly. Since 1938 the Lurgi Ges. für Wärmetechnik m. b. H. has been working on a process that changes the poisonous CO with a small amount of the H_2 in the gas into a more valuable Fischer-Tropsch product. In most cases the detoxified gas is cheaper, since the net excess for the production of hydrocarbons, in general, exceeds the cost of the used gas. This method, therefore, is of great interest, since it places gas detoxification on an economical basis. Especially favorable is the relation in the working up of city gas from the Lurgi pressure gasification plants since this gas possesses a relatively high CO content of 15–20% and a favorable pressure of 20 atm. for the catalytic conversion to hydrocarbons. Special Fe catalysts are used which need for the reaction, beside CO, only a little H_2. Because of the equalizing effect in the gas contraction associated with the reaction the H_2 content in the detoxified gas remains virtually the same, and the end gas still corresponds to a normal city gas. In 1942 the process was experimentally tested at Bohlen near Leipzig on a large scale processing 1,600 *N* m.³ of gas per hr. Several months operation showed that, depending on the catalyst compostion and the operating conditions, mainly paraffin or low-boiling hydrocarbons could be obtained. Since CH_4 formation in the synthesis is favorable to the city gas, the yield per *N* m.³ of gas used, is far above 200 gm.

1272. Grounds, A. Review of Work on the Production of Oils—the Fischer-Tropsch Process. Chem. Age, vol. 38, 1938, p. 164.

Reviews development of synthesis of liquid fuels from the early discoveries of Sabatier in 1902. Fischer and Tropsch, working together since 1922–23, first established that, in the presence of an alkaline Fe catalyst at 400° C., and at a pressure of 100 atm., alcohols, aldehydes, ketones, and fatty acids could be produced. 17 different compounds were isolated in this early work, and the mixture of these compounds was called Synthol. With Zerbe, Fischer found that, as lower pressures were used, compounds containing less O were formed and that the rate of the reaction decreased. Eventually, it was found that, at 7 atm. pressure, an oil was produced consisting principally of hydrocarbons of a paraffinoid nature. In 1905, Fischer and Tropsch found that the reaction could be carried on at atmospheric pressure; they also discovered that, if the catalyst was to have a long life, it would be necessary to work at temperatures of 200°–300° C. With a reduction in temperature the reaction was slowed still further, so that new and more highly active catalysts had to be found. Tropsch left Fischer in 1928 to found the new Institute for Coal Research at Prague, and it took Fischer and his co-workers (Koch and Meyer) 6 yr. to produce catalysts that were active enough at 200° C. and at atmospheric pressure and yet had a reasonably long life. It was found that the presence of a strong alkali brought about polymerization, until eventually solid paraffin instead of liquid oils was obtained as an end product. Eventually a Co–Th catalyst was produced, which was found not only to give high yields of liquid products, but which also had a long life in actual practice. The theoretical yield of liquid products was actually 185 gm. per m.³ of gas, containing 29.5% of CO and 60% H_2. The latest reports showed that 151 gm. per m.³ could be obtained, corresponding to a conversion of 81.6% of the total material. This result was brought about with the use of a 2-stage operation at 190° C. and 184° C., respectively, using a Co–Cu–Th–kieselguhr catalyst. One of the essentials for satisfactory operation of the Fischer-Tropsch synthesis was purification of the synthesis gas from organic S compounds. A method had been elaborated by Fischer and his collaborator Roelen, which was found to be perfectly satisfactory in industrial practice and which was capable of reducing the organic S in the gas to the abnormally low figure of 0.2 gm. per 100 m.³ or 0.087 grain per 100 cu. ft. The synthesis of liquid products from CO–H_2 was an exothermic reaction. The heat generated raised the temperature of the gases several hundred degrees. The conversion vessels were surrounded by a circulating oil system, so that the oil picked up the heat evolved and transmitted it to H_2O for the generating of steam in a special-type boiler. The products formed by the synthesis were water-white. Before use they were freed from traces of organic acids by a light soda wash. The products were free from S. The remarkable flexibility of the Fischer-Tropsch process from the point of view of the raw material available was stressed, and the yield of finished products from the primary oils obtained was given as: Gasol (consisting mainly of C_4H_{10} and C_3H_8), 8%; petrol, 50%; diesel oil, 39%; and soft paraffin wax, 3%. In addition, a hard paraffin wax was recovered from the catalyst mass during regeneration. This wax almost paid for the cost of regeneration of the catalyst. It was shown how the octane number of the petrol produced could be improved by cracking and by blending with benzol and/or alcohol, together with the addition of $PbEt_4$.

Grummer, M. *See* abs. 2098, 2099, 2100, 2101, 2102, 2103, 2103a.

1273. Grundmann, C. [Nitration of Higher-Molecular Paraffin Hydrocarbons.] Die Chemie, vol. 56, 1943, pp. 159–163; Great Britain Fuel Research Intel., No. 5, July 1944; Oel u. Kohle, Erdoel, Teer, vol. 40, 1944, p. 227.

Charging stocks employed included mixtures of liquid hydrocarbons from the Fischer-Tropsch synthesis.

1274. Gruner, L. O. [Motor Fuels.] Tek. Ukeblad, vol. 85, 1938, pp. 383–389, 400–403, 411–413.

Surveys the motor-fuel problem and the possibilities of synthetic fuel production as they affect Norway, with special reference to the use of the cheap electric power available. Petroleum refining, hydrogenation, the Fischer-Tropsch synthesis, and the use of NH_3 as fuel are discussed.

1275. Guelpérine, N. L., and Naiditch, I. M. ["*I–S*" Diagrams for H_2, CO, N_2, N_2+3H_2 and $CO+2H_2$.] Chim. et ind. vol. 34, 1935, pp. 1011–1020, 1279–1288; Chem. Abs., vol. 30, 1936, p. 2064.

Diagrams are presented for pressures up to 1,000 atm. and temperatures <600°. They were constructed from experimental data on compression and thermal capacities found in the literature, including the low-temperature and relatively low pressure curves of Keesom and Houthoff for H_2 and N_2. The diagrams are not absolutely accurate but are sufficiently so for use in synthetic-NH_3, synthetic-MeOH, and oil-cracking industries.

1276. Guertler, W. [Investigations of Vittorf and Hanemann Relative to the Carbides of Iron.] Internat. Ztschr. Metallog., vol. 5, 1913, pp. 239–277; Chem. Abs., vol. 8, 1914, p. 1407.

Discusses status of the Fe–C system.

1277. ———. [Law Governing the Transformations of the Carbide System Into the Graphite System.] Stahl u. Eisen, vol. 34, 1914, pp. 520–525, 751–754; Chem. Abs., vol. 8, 1914, p. 3002.

Discusses Fe–C diagram in detail. Fe_3C is unstable at all ordinary temperatures, but the transformation energy is so weak that it must be heated for hours at 800° before it breaks down. With increases in temperature, the time required for decomposition is shorter. In spite of the instability of Fe_3C, it is possible, under certain conditions, to cause the reaction $Fe_3C=3Fe+C$ to reverse. If the tendency to form graphite is stronger than the force tending to decompose Fe_3C, the speed of the reaction is governed by the former force. There is some doubt as to which of these forces is influenced by the presence of Si. The separation of graphite is accompanied by increase in volume; consequently, its formation is retarded by pressure. The main factor is, however, temperature, and it is by varying this that foundries obtain the various results they desire. Gives diagram that shows graphically the relative amounts of free and combined C with different temperatures; by means of it the changes during cooling are discussed.

Guest, P. G. *See* abs. 1449.

1278. Guillaud, C. [Ferromagnetic Properties of the Compounds Manganese-Nickel Alloy and Cementite.] Compt. rend., vol. 219, 1944, pp. 614–616; Chem. Abs., vol. 40, 1946, p. 1711.

Alloys of Mn with Ni containing 57–85 atomic % of Ni are paramagnetic when tempered and ferromagnetic when annealed. The most strongly ferromagnetic alloy corresponds to the composition $MnNi_3$. This was prepared by fusing pure Mn (99.98%) and pure Ni (99.76%) in an Al_2O_3 crucible in a high-frequency furnace. To obtain the maximum magnetization the specimens were annealed for 3 wk. at approximately 470°. At 480°, $MnNi_3$ is no longer ferromagnetic. The change is not completely reversible, and the alloy is paramagnetic or weakly ferromagnetic depending on the speed of cooling to a temperature below 480°. In the case of ferromagnetism the spontaneous magnetization reappears at 480°. This indicates probably the simultaneous existence of a Curie point and a point of transformation. Curves are given showing the specific magnetization as a function of T^2 and the law of approach to saturation at 290° K. and 0° K. as a function of the reciprocal of the internal field. For 0° *K.*, $\sigma_\infty=98.16$. Curves are also given showing the results obtained on an exceptionally pure specimen of Fe_3C from which the value $\sigma_\infty=169.3$ at 0° K, is deduced.

1279. Guillaud, C., Michel, A., Bénard, J. and Fallot, M. [Ferromagnetic Properties of Chromium Dioxide.] Compt, rend., vol. 219, 1944, pp. 58–60; Chem. Abs., vol. 40, 1946, p. 2365.

Ferromagnetic CrO_2 was prepared by heating CrO_2Cl_2. This gave a mixture of approximately equal parts of CrO_2 and a solid solution of O_2 in Cr_2O_3 corresponding to $(8\ Cr_2O_3+O)$. The exact proportions of the 2 constituents in a particular specimen were deduced from its loss in weight when the whole was converted into Cr_2O_3 by calcining at 900°. Magnetic studies made on 2 specimens with different CrO_2 contents, prepared independently, are reported as giving concordant results, although no experimental details are given.

1280. Guillaumeron, P. [Chemical Applications of Natural Gas in the United States.] Génie civil, vol. 124, 1947, pp. 125–130.

Review in which the Fischer-Tropsch process is mentioned.

1281. Guillemin, A. [Corrosion of Metals by Methanol.] Ann. chim. vol. 19, 1944, pp. 145–201; Chem. Abs. vol. 40, 1946, p. 1437–1438.

Corrosion of metals by MeOH was studied at room temperature. Al, Cu, Sn, Pb, Zn, Cd, Sb, Bi, Cr, Fe, Ni, Co were subjected during 4 months to anhydrous MeOH, MeOH containing 20% H_2O, MeOH containing 2% CH_2O, MeOH containing 1% HCOOH, and 1%

X-ray examinations by the powder method have been made of Fe nitrides prepared by passing NH_3 over pure Fe, which was prepared by reducing Fe oxides with H_2. The structure is dependent only on the N content and not on the method or conditions of preparation. The maximum N content is 11.3%. The nitrides are really solid solutions of N in Fe. At 0.2% N, faint lines of a face-centered cubic lattice begin to appear; all α-Fe lines have disappeared at 5.7% N. The new lines remain fixed as N increases and indicate a unit cube of edge 3.789 Å. U. somewhat larger than that of γ–Fe. However this is called γ–phase and is considered to be a solid solution of N in γ–Fe. The Fe atoms are in a close-packed cubic array, with N atoms in the interstices. No evidence that the N atoms are regularly arranged appears. A new phase, ϵ, appears at 5.7–6.1% N. It is hexagonal and close-packed, the unit cell remaining fixed in size at first, but beginning to increase at 7.3–8.6% N. The phase is estimated to become homogeneous at 7.5–8% N. The ϵ parameters are the a=2.695 Å. U., c=4.362 Å. U. Increase in N increases the parameters, c increasing relatively less than a. The ϵ phase is a solid solution of N in hexagonal close-packed Fe. A thin Fe sheet nitrided at 450° for 4 hr. showed strong γ and weak ϵ lines.

1306. ———. [Metallic Nitrides, Carbides, Borides. and Hydrides.] Metallwirtschaft, vol. 10, 1931, pp. 387–390; Chem. Abs., vol. 25, 1931. p. 4192.

Discussion of the chemical and physical properties of the nitrides, carbides, borides, and hydrides of the metallic elements, particularly as related to the lattice structure of these compounds. Special attention is given to the compounds of these elements with such transitional metals as V, Cr, Ti, Mn, Fe, Co, Ni, Mo, W, Os, Ir, Pt, U. The nitrides, borides, carbides, and hydrides of these metals exhibit strongly metallic properties, while analogous compounds with the other metals are nonmetallic in nature. The lattice structure of these transitional elements seems to be characterized by an electron defect, and this together with the small atomic radii of the metalloids in question seem to be a factor in the metallic nature of these compounds.

1307. ———. [Regularity in Crystal Structure in Hydrides, Borides, Carbides and Nitrides of Transition Elements.] Ztschr. physik. Chem., vol. 12, B, 1931, pp. 33–56; Chem. Abs., vol. 25, 1931, p. 2615.

Structure of crystals of binary compounds containing a so-called "transition element" and H, B, C, or N is critically examined with respect to the ratio of atomic radii. If this ratio $r_m : r_x > 1.7$ the structure is simple, while if the ratio is smaller, the structure becomes more complex the smaller the radius of metal ion. Only these combinations show a typical metallic character in crystal structure, which is termed an infiltration structure. The latter shows a combination M_4X, M_2X, MX, and MX_2, each of which is described. The face-centered cubic or close-packing hexagonal lattice, both of coordination number 12 are most often observed. 1 case each of body-centered cubic and simple hexagonal, both of coordination number 8, was found. Careful discussion follows of the packing arrangement of atoms and the relation to coordination numbers.

1308. ———. [Powder Photographs of a New Iron Carbide.] Ztschr. Krist., vol. 89, 1934, pp. 92–94. Chem. Abs., vol. 28, 1934, p. 7100.

X-ray patterns of Fe that had been in contact with CO for 430 hr. at 225° show weak lines of Fe_3O_4 and Fe_3C, with stronger lines of a new carbide, which is probably Fe_2C. At higher temperatures the Fe_3C grows at the expense of the Fe_2C. After heating *in vacuo* at 500°, only lines of Fe_3C remain. It was not found possible to index the lines of the pattern for Fe_2C.

1309. ———. [Crystal Structure of Magnetic Ferric Oxide, γ–Fe_2O_3.] Ztschr. physik. Chem., vol. 29, B, 1935, pp. 95–103; Chem. Abs., vol. 29, 1935, p. 6122.

When Fe_3O_4 is oxidized at low temperature, the spinel structure is retained to form γ–Fe_2O_3 with a steady decrease in the dimension of the elementary cell from 8.380 to 8.322 Å. Change in intensity of the X-ray patterns and the density indicates that the increase in the O concentration produces empty spaces in the spinel lattice so that in γ–Fe_2O_3, where the O concentration reaches a maximum, ⅙ of the original Fe atomic positions are unoccupied, and the elementary cell contains an average of 21⅓ Fe and 32 O.

HAHN, D. A. *See* abs. **2173.**

HAHN, H., AND MÜHLBERG, H. [Metal Amides and Metal Nitrides. XX. System Iron–Nickel–Nitrogen.] *See* abs. **1650.**

1310. HAHN, O. [Contribution to the Thermodynamics of Water Gas.] Ztschr, physik. Chem., vol. 44, 1903, pp. 513–547; Chem. Zentralb., 1903, 2, p. 540; Jour. Soc. Chem. Ind. (London), vol. 22, 1903, p. 1038.

From the results of experiments, at a constant temperature with mixtures containing varying proportions of CO_2 and H_2 the author finds that the law of mass action can be applied for the reaction:

$$CO_2+H_2=CO+H_2O.$$

The value of equilibrium-constant K $\left(=\frac{CO.H_2O}{CO_2.H_2}\right)$ is 0·534 at 686°C., 0·840 at 786°, 1·197 at 886°, 1·571 at 986°, 1·62 at 1.005°, 1·96 at 1,086°, 2·12 at 1,205°, and 2·49 at 1,405°. Up to 1,100° C. the constant may be expressed by the formula: $\log K=-\frac{2232}{T}-0{\cdot}08463 \log T-0{\cdot}0002203\,T+2{\cdot}5084$.

1311. ———. [Equilibrium $CO+H_2O=CO_2+H_2$.] Ztschr. physik. Chem., vol. 48, 1904, pp. 735–738; Jour. Chem. Soc., vol. 86, 1904, (2), p. 643A.

1312. HAKANSON, H. [Production of Motor Fuels.] Tek. Tid. Uppl. D. Mekanik, Skeppsbyggnadskonst Flygtek., Automobil Motortek., vol. 70, 1940, No. 8, pp. 74–76; No. 42, pp. 77–84; No. 46, pp. 85–89; No. 51, pp. 98–100.

Discussion on the production of motor fuels from petroleum and from coal by carbonization, distillation, hydrogenation, gasification, and the Fischer-Tropsch synthesis.

1313. HALE, C. H. Rapid Analysis of Fischer Synthesis Catalyst. Petrol Refiner, vol. 25, No. 6, 1946, pp. 117–120.

Describes methods that have been found most satisfactory for the determining Co and Th in Fischer synthesis catalyst. The procedure for Co involves titration in an ammoniacal solution with $K_3Fe(CN)_6$. The end point is detected by means of the dead-stop technic. The method is very rapid and accurate and is not subject to interference by any of the other materials commonly associated with Co. Th is precipitated as the iodate. The $Th(IO_3)_4$ is dissolved, reacted with iodide, and the liberated iodine titrated with thiosulfate ($Na_2S_2O_3$). The method is more rapid and equally as accurate as the gravimetric method involving precipitation of thorium oxalate.

1314. HALL, C. C. Chemische Werke Essener Steinkohle A.-G. Bergkamen Near Kamen-Dortmund, Germany. Inspection of Fischer-Tropsch Plant. CIOS Rept. XXVII–54, 1945, 5 pp. PB 413; TOM Rept. 10; TAC Rept.SnMC–4; TOM Reel 197.

This plant contained 124 standard-type atmospheric-pressure ovens, divided into 2 stages; the exact distribution between them depended on catalyst life, plant operation, etc. Each oven contained 1 ton of Co catalyst, the life of which was about 8.5 mo. The synthesis gas was prepared from coke and coke-oven gas in 12 Demag water-gas sets and contained CO, 29% and H_2, 59%. A freshly charged oven was treated 1st at 185°–190° for 24–48 hr. with residual gas from stage 2 and then put on stream in stage 2 at 180° where it remained for 2–3 mo. It was then transferred to stage 1 when the operating temperature had risen to about 190°. The gas contraction in stage 1 was 45–50% and the over-all contraction 72–75%. The average annual yield of products was 156–157 gm. per m.³ of gas. After 2–3 mo. in stage 2 and 3 weeks in stage 1, re-activation of the catalyst took place by means of H_2 treatment at 195° for 24 hr. alternated with solvent extraction with benzine at 120°–150°. The products of the process were: 14.7% gasol, 47.9 gasoline, 17.3 diesel oil. 10.7 heavy oil, 7.7 gatsch, and 1.7 hard wax from catalyst. The annual output was 80,000 ton. The composition of residual gas from the process (500,000 m.³ per day) was: CO_2, 20.3%; C_nH_m, 1.6; O_2, 0.1: CO, 10.5; H_2, 18.0; CH_4, 30.9; N_2, 18.5%.

1315. ———. Fischer-Tropsch Catalyst Ovens and General Information on the Fischer-Tropsch Process Obtained at Offices of Gutehoffnungshütte A.-G., Sterkrade. Ruhr. CIOS Sept. XXVII–70. 1945. 5 pp.; PB 975; TOM Rept. 37; TOM Reel 197; TAC Rept. SnMC–10.

3 firms controlled the manufacture of Fischer-Tropsch ovens: Mannesmanne Rohrwerke, Krupps. and Gutehoffnungshütte, the former being the largest manufacturer. There were 3 types: (1) The normal Lamellanofen for use at atmospheric pressure: (2) the double-tube oven for medium pressure, Co-catalyst synthesis: and (3) the double-tube oven designed for use at 20 atm. pressure for the Fe-catalyst synthesis and of the same size and catalyst capacity as (2). Each oven contained 2,100 double tubes. The construction is shown in sketch.

1316. ———. The Fischer-Tropsch Process. Jour. Imp. Coll. Chem. Eng. Soc., vol. 1, 1945, pp. 15–20; Fuel Abs. 5105, November 1945.

Briefly discusses historical background and characteristics of process. Production of synthesis gas and its purification are outlined. The synthesis reaction is described, with various suggested improvements, which have appeared in the literature. Discusses condensation, recovery, and utilization of products. A section is devoted to the efficiency and economics of the process.

1317. ———. Oils and Waxes From Coal—Recent German Work on Catalysts. Chem. Age, vol. 55, 1946, pp. 569–570; Colliery Guard., vol. 173, 1946. pp. 698–700; Chem. Trade Jour., vol. 119, 1946, pp. 729–730; Ind. Chemist, 1946, pp. 761–763; Jour. Inst. Fuel, vol. 20, 1947, pp. 65–76, 95.

Lecture presented before a joint meeting of the Society of Chemical Industry and the Institute of Fuel. The Fischer-Tropsch process was operated in 9 plants in Germany having an annual capacity of 740,000 ton of hydrocarbon products but a maximum output of only 570,000 ton. The catalyst used throughout the plants was of the standard type Co 100 : ThO_2 5 : MgO 8 : kieselguhr 200; research during the last years was concerned with development of the Fe catalyst, and the general trend was toward the production of olefins, waxes, and alcohols for chemical use rather than products for fuel use. The general efficiency of the process and plants was low; not more than 30% of the total heat input was recovered as primary products, with an additional 25% as steam and residual gas. The net heat consumed in producing 1 ton of primary products was equivalent to 4.5 tons of coal. On the basis of 10 RM per £, the capital cost of the German plants varied from 450 to 850 RM per ton annual production and the operating cost, including capital charges, from 240 to 390 RM per ton of primary products. The manufacture of synthesis gas was the major item of cost; to improve the economic prospects of the process 2 possibilities exist: The utilization of a high proportion of the products as high-priced chemical products and a reduction in the cost of synthesis gas. It is estimated that the production of the primary products under present-day British conditions would cost between 2s. and 2s. 6d/gal.

1318. ———. Summary of Information on Fischer-Tropsch Waxes. BIOS Rept. 1831, 1946, pp. 284–303.

See abs. **444.**

1319. ———. Chemical Products From the Fischer-Tropsch Process. Chem. and Ind., 1947, p. 722; Chem. Age, vol. 57, 1947, p. 701.

Abstract of paper read before the Glasgow Section, Society of Chemical Industry. With Co catalysts, the formation of straight-chain aliphatic hydrocarbons is favored, whereas Fe catalysts promote the production of alcohols. The general range of products was discussed under the heads of fuels, waxes, lubricating oils, alcohols, fatty acids, detergents, etc. The most interesting chemicals are the primary alcohols and the fatty acids. The prospects for operating the Fischer-Tropsch process in Britain are not bright for the production of fuels, but there is some hope of operation for the production of chemicals in competition with similar products from petroleum.

1320. ———. Fischer-Tropsch Process as a Source of Synthetic Products. Gas World, vol. 57, 1947, p. 47.

Paper presented at the St. Andrews symposium. This process may be used for converting coal into liquid fuels or into a variety of aliphatic products. Only the latter application is of immediate economic interest to Great Britain. It is believed possible to operate the process so as to produce materials of the type of hydrocarbon waxes, lubricating oils, long-chain alcohols, fatty acids, and detergents as a major proportion of the entire output with liquid fuels as relatively minor products.

1321. ———. Fischer-Tropsch Process—Present Position and Future Possibilities. Gas World, vol. 126, 1947, pp. 58–64; Iron and Coal Trades Rev., vol. 154, 1947, p. 62; Gas Times, vol. 50, 1947, pp. 37–38, 40–42; Engineering, vol. 163, 1947, pp. 30, 54–55, 79; Inst. Fuel (London) Bull., April 1947, pp. 97–99, 113; Ind. chim., vol. 34, 1947, pp. 127–129.

Abridged version of paper presented before the Yorkshire Section of the Institute of Fuel. The major part of the paper is taken up with a discussion of the operation of the process in Germany, including performance data, composition of the reaction products for both the normal- and medium-pressure processes, and the thermal efficiency. Mentions experimental departures from the orthodox method of carrying out the process with the viewpoint of improving its efficiency or increasing the range of the products. Makes an attempt to compare German costs with British conditions. Taking the cost of coke for synthesis-gas manufacture at 3£ per ton and converting the other costs on the basis of 10RM=1£, the total production cost for the medium-pressure process as operated in Germany would be 32£ per ton or 2s.1.5d. per gal. of primary product. Assuming a production of and a revenue from a ton of primary product to be as follows: 0.10 ton liquefied gas at 10£ per ton; 0.50 ton gasoline and diesel oil at 18£ per ton; 0.13 ton Kogasin at 30£ per ton; 0.17 ton soft wax (Gatsch) at 28£ per ton; and 0.10 ton hard wax at 60£ per ton the income would be 24.7£, or a loss of 7.3£ per ton of primary products. The conclusion is therefore made that the operation of the process in England would not be economical or profitable. To make it attractive, certain improvements would have to be made: The cost of synthesis gas must be reduced, the synthesis process must be improved either in the direction of in-aqueous HCOOH. Most of the metals were of 99.9+% purity, Ni 99.8%, Cd 99.5+%, Bi 99–100%, Co 98–99%. Pure MeOH attacked only Pb, Sb, Al, and Sn. In the presence of 20% water Al and Sn are protected by an oxide layer and are not attacked; the corrosion of Pb is reduced; Zn, Cd, Fe, and Co are attacked. Only Pb and Sb are attacked by MeOH containing 2% CH_2O·MeOH containing 1% HCOOH corrodes most metals, particularly Pb, Zn, Cd, Fe, Ni, Co, Cu, and Sb. Al is barely attacked, and Cr, Sn, Bi are not attacked. In 1% aqueous HCOOH solution Cu is not attacked; Pb is attacked much less than in MeOH solution; the corrosion of Al is much stronger; and Sn and Bi are slightly attacked. The results are tabulated and expressed in weight loss per 100 gm., and weight loss per 100 cm.^{2} The experiments were carried out in the dark. The apparent importance of the presence of HCOOH led to the study of the mechanism of the corrosion of Fe, Zn, and Cu by MeOH containing traces of that acid. In the presence of air MeOH containing HCOOH reacts with Fe with formation of dimethoxyferric formate, $HCOOFe(OMe)_2$ (I). In an anhydrous solution Zn forms a basic formate, 4(HCOOZnOH)·–ZnO, and in the presence of water a neutral hydrate, $(HCOO)_2Zn \cdot 2H_2O$. Cu forms a mixture of basic formates. In the absence of air Fe dissolves with formation of neutral ferrous formate: Zn is not attacked; Cu is protected by the formation of an insoluble cuprous formate. Zn and Cu undergo surface oxidation. The formation of $Pb(OMe)_2$ is attributed to an initial surface oxidation: in the absence of air Pb is not attacked by MeOH. (I) was successively hydrolyzed to ferric dihydroxyformate, $HCOOFe(OH)_2$, and to the neutral formate and $Fe(OH)_3$. Calcination at 250° of (I) gave pure, pyrophoric Fe. The complete hydrolysis of the basic Zn formate gave neutral Zn formate and $Zn(OH)_2$. In the presence of sunlight or ultraviolet radiation, Fe is attacked by pure MeOH with formation of (I): this proves that MeOH is partly oxidized to HCOOH. In MeOH containing HCOOH bronzes and Al bronzes were etched (this can serve for micrographic studies); steel containing 13% Cr was not attacked: steel containing 12% Ni was attacked less than steels containing 2%, 3%, 5% Ni; the latter were attacked as repidly as pure Fe.

GUIOT-GUILLAN, G. *See* abs. 1055.

1282. GUISELIN, A. [From the Theory to the Realization of Synthetic Fuels. VI. The Fischer Process.] Chaleur et ind., vol. 5, Special No., December 1924, pp. 97, 133–134, 162.

Brief statement, within a long discourse, of the production of synthol and synthine by passing water gas through a catalyst of Fe turnings and K_2CO_3 at a temperature 390°–430° and a pressure 100–150 atm.

1283. GULBRANSEN, E. A. Transition-State Theory of the Formation of Thin Oxide Films on Metals. Trans. Electrochem. Soc., vol. 83, 1943, 13 pp.; Chem. Abs., vol. 37, 1943, p. 2251.

Transition-state theory of diffusion was applied to the rate of oxidation of metals as a function of temperature. The expression involves an entropy of activation as well as the energy of activation. Experimental results indicate that the oxidation of Fe, stainless steel, and Cu follows the parabolic law for certain temperature ranges and pressure ranges after a certain initial period. The parabolic-rate-law constants are shown to follow a straight line when log K is plotted against $1/T$. Energies of activation of 22,600, 29,600 and 24,900 are found for Fe, stainless steel, and Cu, respectively. Entropies of activation are calculated to be −31, −35, and −6.8 for Fe, stainless steel, and Cu, respectively. The importance of entropy factor is briefly considered.

1284. GULBRANSEN, E. A., AND RUKA, R. Kinetics of Solid-Phase Reactions in Oxide Films on Iron. Reversible Transformation at or Near 570°. Jour. Metals, vol. 188. Trans., 1950, pp. 1500–1508; Chem. Abs., vol. 45, 1951, p. 426.

Forward and reverse reactions, $Fe_3O_4 + Fe \rightleftharpoons 4\,FeO$, were studied by electron-diffraction methods. In thin films the forward reaction occurs at temperatures 170° below the equilibrium value. The mechanism of the forward reaction is governed by the diffusion of Fe. Studies of the reverse reaction as a function of time, temperature, and oxide composition indicate that a process of nucleation and growth is rate controlling.

1285. GULF RESEARCH & DEVELOPMENT COMPANY. General Summary of Economic Data. Synthetic Liquid Fuels Hearings Before a Subcommitte of the Committee on Public Lands and Surveys, U. S. Senate. 78th Cong., 1st sess., on S. 1243, 1944.

This summary of data is taken from a "Literature Survey on the Fischer-Tropsch Synthesis of Hydrocarbons," January 1940–December 1943, of the Gulf Research & Development Co. Chemistry Division Rept. 260, April 15, 1944.

General summary of cost data for synthetic liquid fuels process[1]

Investment	From coal hydrogenation	From Fischer-Tropsch synthesis, using coal	From Fischer-Tropsch synthesis, using natural gas	From oil shales	From petroleum
($/day bbl.)	7,500–14,300	6,180[2]–16,667	2,200–4,767	375–3,000	700.
Operating costs[3] (¢/gal.)	15.5[2]–25	18.2[2]–24.4	4.8[2]–17.4	([1])–10.7	5–6.
Total raw materials required (ton/bbl.).	Coal: 0.5[2]–1.25	Coal: 0.7	Natural gas: 0.22–0.25	Oil shale: 0.9–2.7	Crude oil: 0.328.
Steel requirements (ton/bbl.).	8.3–14.1	8.9–14	2.8–6.5	1.3–([1])	0.7.
U. S. reserves of raw material.	Coal: 3.2 trillion ton (3,000 yr.).	Coal: 3.2 trillion ton (3,000 yr.).	Natural gas: 85–170[2] trillion cu. ft. (30 yr.).	Shale oil: 92 billion bbl. (65 yr.).	Oil: 20–21 billion bbl. (14 yr.).

[1] Data presented represent testimony extremes. In 2 cases, it appears that truly representative ranges were not given.

[2] Trend of testimony indicated that the most probable figure was of this order, although perhaps somewhat higher or lower. For operating costs by the first 2 methods, eventual estimates are somewhat lower.

[3] Including depreciation. Figures are presumably for 70–75 octane-number gasolines.

1286 ———. Literature Survey on the Synthine Process, January 1944–January 1945. Chemistry Division Rept. 295, 1945, 70 pp.

Annotated bibliography.

1286a. GUMZ, W. [Present Status and Future Possibilities in Gasification Processes.] Gas- u. Wasserfach, vol. 88, 1947, pp. 129–136; Chem. Abs., vol. 42, 1948, p. 4,729.

Trend of gas production is in the direction of complete gasification with the use of noncoking coals. Water-gas generators are commonly used for synthesis-gas production; the use of O_2 is advantageous when this can be generated at a low price. A greatly expanded use of producer gas is seen particularly in steel works owing to the tendency to sell coke-oven gas to super-gas schemes. The Flesch-Winkler gas producer serves as a transition stage between the grate-type producer and the powdered-coal gas producers. In this generator a 1-m. layer of fine fuel is held on a grate by an air pressure of about 4 mm. H_2O column. This is gasified for 10–15 min. until a slag layer is formed, which is caused to sink to the grate by introducing steam; this slag is then removed by means of a H_2O-cooled stirring arm. The slag removal period requires 1–3 min., which is followed by a purge of 1 min. after which fresh fuel is introduced and gasification continued. Low-grade high-ash fuels are used. The slagging-type producer offers considerable promise for low-grade fuels, especially when combined with metal recovery. A dry air blast is ordinarily used, but this producer can be operated with 2 stages, the upper using saturated air and the lower dry air.

1286b. ———. Gasification of Solid Fuels at Elevated Pressures. Ind. Eng. Chem., vol. 44, 1952, pp. 1071–1074.

Effect of pressure on the gasification of solid fuels is investigated by calculation and by evaluation of experimental data. A method of calculation is presented based on the C, H_2, O_2, N_2 and S balances, and on the equilibrium constants of the gasification reactions. Previously published methods have been extended to apply to the behavior of S during gasification. An increase in pressure shifts the Boudouard reaction, the heterogeneous water-gas reaction, and CH_4 formation toward increased CO_2, H_2O, CH_4 content and higher equilibrium temperature. S appears mainly as H_2S in the product gas. Other forms of S such as organic S and S vapor can occur only at extremely high pressures and in the absence of moisture. This fact permits a simplified method of calculation, assuming that S occurs only as H_2S. The increase in equilibrium temperature keeps gas quality nearly constant up to 10 atm. and allows higher steam and lower O_2 content in the blast at higher pressures. Effect of absolute pressure on pressure drop through the fuel bed is calculated and the calculations are supported by experimental results. Pressure drop is a simple function of pressure and is inversely proportional to the absolute mean pressure in the reactor. Elevated pressure has no effect on the terminal velocity of fuel particles in suspension in the range of validity of Stokes' law, but the terminal velocity decreases proportionately to $1/\sqrt{P}$ in the Newton range (constant resistance factor). Formulas are given for the terminal velocity within the transition range of Reynolds numbers; they can be used to estimate carryover losses and the effect on reaction rates of pulverized-coal gasification. Pressurizing is applicable to various coal-gasification processes; it has been applied to the manufacture of high-B. t. u. gas, and it has good prospects for playing a major role in synthesis-gas production and power gas for steam boilers and gas turbines.

1287. GUMZ, W., AND LESSING, R. [Processes for the Manufacture of Synthetic Gas.] Ztschr. Ver. deut. Ing., Beih. Folge No. 2, 1940, pp. 36–42; Chem. Abs., vol. 34, 1940, p. 6794.

Comprehensive summary, with diagrams, data, and 46 refs.

1287a. GUNDERMANN, E. [Residues From Distillation of Synthetic Fatty Acids (Oxide Pitches).] Bitumen, Terre, Asphalte, Peche. vol. 5, 1951, pp. 114–117; British Abs., 1951, B, I, p. 1202.

In Germany fatty acids are produced by oxidation of Fischer-Tropsch slack wax (b. p. >350°) containing the maximum amount of C_{25}–C_{35} paraffins. The oxidized product contains 30–35% of mixed fatty acids and aldehydes, alcohols, dicarboxylic acids, ketones. The complex mixture of acids is separated by conventional methods and fractionally distilled in a vacuum into C_4–C_9 fatty acids and C_{10}–C_{20} (soap) fatty acids. The residue of oxide pitch (7–15% of the original mixture) resembles tar or pitch; extensive distillation does not produce a hard pitch. The material reacts with S to form materials of high molecular weight, the rise in softening point depending on the amount of S, reaction time and temperature; the maximum reaction temperature is 190°–200°. With 10% of S, polymerization mainly occurs; with 20% of S, crosslinking with combination of S takes place and infusible products are formed. Addition of 5% of 62% HNO_3 to oxide pitch has a pronounced polymerizing effect. The S and HNO_3 products of the pitch are gummy and tough but are not hard.

1288. GUNNESS, R. C. Future Liquid Fuels. Chem. and Eng. News, vol. 26, 1947, pp. 2123–2127, 2171; Chem. Abs., vol. 42, 1948, p. 6509.

During 1947 the United States used about 5.8 million bbl. of petroleum/day. 25 yr. ago about 27% of each bbl. of crude oil was made into gasoline, last year over 40%, while a 75% yield could be produced if this were the only product required. The gasoline demand has increased 20% over 1941 and 7% over 1946 but is believed to be slowing up. Most of the increase in fuel consumption in recent years has been oil. Petroleum demands in 1970 are established at 7,130 bbl. per day, of which 3,160 bbl. will be motor fuel. Diesel fuel will also be used more widely by the railroads and for heavy motor vehicles; changes in the fuel may be required, which must be tested in service engines rather than in the laboratory. Present known crude petroleum reserves are equal to about 12 yr. consumption at the present rate, but more reserves were found last year than were used. Imports, especially from the middle east, will be required to maintain reasonable reserves. The immediate production of large quantities of synthetic fuels from coal would be very expensive; much more research is required. A modified Fischer-Tropsch process, with natural gas as the raw material, will soon be in production in several plants. The hydrocarbons produced in this synthesis consist principally of straight-chain compounds ranging from CH_4 to solid waxes. The major portion of this product is unsaturated in structure (in contrast to results obtained with the German Co catalyst) and can be refined to give a gasoline with an octane number of about 80, and heavier refined products comparing favorably with those from petroleum. In a plant producing 6,000 bbl. per day of synthetic hydrocarbons, the established yield of other organic chemicals is about 420,000 lb. per day. This will be a major source for these compounds, which will be separated and purified at plants near the hydrocarbon-synthesis plants. Gasoline quality requirements will improve, and cars having octane requirements of 95 or even higher are planned for the future. Even with decreasing demands per car, the increased number of cars will require more gasoline. The cost of this improved fuel will be greater. The gas turbine probably will require a clean distillate oil for fuel. The fraction of the motor fuel produced by synthesis will be small for some time but will increase with demand. Residual fuel-oil supply can be expected gradually to decrease, so that coal will be called on to handle an increasing share of the expanding industrial fuel load. Enough high-quality liquid fuels will be available to meet all demands most efficiently served by petroleum fuels.

———. *See* abs. 372.

1289. GUNTERMANN, W. [Gasification of Solid Fuels.] Wärme, vol. 59, May 9, 1936, pp. 321–323.

Discusses matters of interest in relation to the production of NH_3, alcohol, oil, and gasoline from substances derived wholly or partially by the gasification of fuels. The Bubiag-Didier, the Drawe, the Winkler, the Lurgi, and the Pintsch-Hillebrand processes are characterized and the gasification prospects in relation to general gas supply, heating gas for industrial purposes, gas for synthetic processes, and for power applications are discussed. Activity is especially pronounced in the field of syntheses, particularly as regards meeting German requirements for motor fuels. The Bergius hydrogenation process and the Fischer synthesis of gasoline require very large quantities of gas, which can be supplied conveniently by the gasification of solid fuels.

1290. Gunther, I. Thesis, Bonn University, 1935, 22 pp.

Contribution to the study of the high-boiling liquid and solid hydrocarbons formed by synthesis from CO and H_2 by the process of F. Fischer and H. Tropsch.

Gusev, V. I. *See* abs. 1586.

Guseva, I. V. *See* abs. 791.

Gustavson, E. *See* abs. 1384.

1291. Guthrie, V. B. Nazis Dropped Fischer-Tropsch Process for Coal Hydrogenation. Nat. Petrol. News, vol. 37, No. 44, 1945, pp. 4, 44, 46.

According to a report of the U. S. Technical Oil Mission, indications are that the Fischer-Tropsch process, as a means for making synthetic liquid fuels and lubricants, was discarded in favor of coal hydrogenation. It appears, however, that the decision to do this was of political rather than scientific nature. The authorities considered that operation of the Fischer-Tropsch process was important from the point of view of the production of chemicals but not of light fuels. Neither was there any evidence of any development that would make the process more attractive economically. It was learned, too, that the German Government had discontinued erection of new Fischer-Tropsch plants early in the war and that the viewpoint existed that the process had not been as successful as anticipated in meeting wartime needs. Development work on the coal-hydrogenation process had been instituted with the prospect of increasing the aromatic content of aviation gasoline, although it did mean some sacrifice in volume yield. Methods were found to operate at 700 atm. pressure in both liquid and vapor phase. The process, known as the D. H. D. process (Dehydrogenation High-Pressure), provides for dehydrogenation of the inferior gasoline from the direct hydrogenation step in an intermittent manner in a series of converters containing a single bed of catalyst consisting of active alumina, on which is deposited 10% of Mo oxide. The final D. H. D. naphtha is said to contain 65–68% of aromatics and is blended back with a corresponding light gasoline fraction to give a finished aviation gasoline with an aromatic content of 40–45% and a minimum octane number of 78 or 87 with 0.09 vol. % of tetraethyl lead. Another interesting point was the manufacture of synthetic lubricating oil from the gas oil or naphtha obtained by the Fischer-Tropsch process. Gas oil is chlorinated, treated with benzol-dichlorethane in the presence of $AlCl_3$, the benzol removed, and the various grades of lubricating oil extracted and processed by conventional methods. In the second process, Fischer-Tropsch gasoline is treated with $AlCl_3$ in special equipment. Another utilization of the Fischer-Tropsch process has to do with the manufacture of higher alcohols by the named Oxo process from olefins; the alcohols were to be used in making soaps and edible fats.

1292. ———. Bureau of Mines Reports. Meager Test Data From Five Years of Synthetic Fuels Research. Petrol. Processing, vol. 5, No. 5, 1950, pp. 505–508, 510.

Critical analysis of the annual 1949 report of the Secretary of the Interior.

1293. Guyer, A. [Gasoline Synthesis.] Bull. Schweiz. electrotech. Ver., vol. 29, 1938, pp. 564–567; Chem. Zentralb., 1939, I, p. 298.

Describes Bergius and Fischer-Tropsch processes and discusses their possibilities for operation in Switzerland.

Gvaliya, T. M. *See* abs. 2890.

Gwathmey, A. T. *See* abs. 2090.

1294. Gwosdz, J. [Theory of Water-Gas Formation.] Ztschr. angew. Chem., vol. 31, I, 1918, pp. 137–140; Jour. Soc. Chem. Ind., vol. 37, 1918, p. 538A; Chem. Abs., vol. 13, 1919, p. 1009.

Experiments were made to ascertain the parts played in water-gas formation by the supposed primary reactions (1) $C+H_2O=CO+H_2$, and (2) $C+2H_2O=CO_2+2H_2$, and the secondary reactions (3) $C+CO_2=2CO$, and (4) $CO+H_2O=CO_2+H_2$. Superheated steam was passed over various forms of heated C and the composition of the issuing gases determined. The temperatures varied from 855° down to 560°, and the speed of the current of steam was also varied. Natural forms of C containing ash in appreciable quantities behaved in a markedly different manner from purified C almost free from ash. With gas coke (8.5% ash) and wood charcoal (1.4% ash), a considerable proportion of CO_2 was always formed (up to 29%). On the other hand, lamp C (0.1% ash) at temperatures down to 600° gave mixtures closely resembling water gas as manufactured. Even at 500° the mixture: CO_2 8.6%, CO 39.5%, H_2 40.0%, residue 11.9% was obtained. It is concluded that reaction (2) cannot be a primary reaction, because reaction (3) is known to be too sluggish to account for the formation of the % of CO found at these low temperatures. It is also concluded that reaction (1) is the primary reaction of water-gas formation, and that the CO formed reacts with the excess of steam tending to establish the water-gas equilibrium and that this reaction is catalytically influenced by the finely divided ash in the C.

1295. ———. [Gasification of Fuels and the Synthesis of Oils.] Erdöl und Teer, vol. 3, 1927, pp. 171–173; Chem. Abs.; vol. 21, p. 1532.

Review and discussion of recent developments.

1296. ———. [Water Gas and the Oil Industry.] Petrol. Ztschr., vol. 24, 1928, pp. 859–870; Chem. Abs., vol. 23, 1929, p. 956.

Reviews methods in use for manufacturing water gas and its uses and relationships to the modern processes for producing synthetic hydrocarbons.

1297. ———. [Production of Hydrogen-Rich Gases for Synthetic Purposes by the Water-Gas Process.] Brennstoff-u. Wärmewirt., vol. 18, 1936, pp. 59–64, 82–85, 96–99; British Chem. Abs., 1936, p. 1187.

Comprehensive review.

H

1298. Haase, —. [Analysis of the Fatty Acids for Soaps, From Tief-Temperatur Hydrierung Paraffin.] FIAT Reel R–19, frames 6668–6685, Aug. 8, 1940; PB 73,594; TOM Reel 261.

Describes extensive analysis of fatty acids obtained from Tief Temperatur Hydrierung paraffin by oxidation. Investigation consists of the following steps: Conversion of the mixed acids into methyl esters; separation of the hydroxy-, keto-, and dicarboxylic esters and their derivatives by adsorption on silica gel; hydrogenation of the olefin carboxylic esters to saturated esters; preliminary and final fractionation of the methyl esters and their saponification. The results show that the fatty acid mixture consists of 15.4% constituents adsorbable on silica gel, 8.1% unsaturated fatty acids, 75.5% straight-chain fatty acids, and 1% branched-chain acids. The C number ranges C_9–C_{22}, includes 2 tables and 9 graphs.

———. *See* abs. 3637.

Haasser, C. *See* abs. 1062.

1299. Haber, F., and Richardt, F. [Equilibrium of Gases in the Bunsen Flame.] Ztschr. anorg. Chem., vol. 38, 1904, pp. 5–64; Jour. Chem. Soc., vol. 86, (2), 1904, p. 166A.

In the inner combustion zone, the equilibrium $CO_2+H_2 \rightleftharpoons CO+H_2O$ is very quickly attained and is not appreciably altered when the gases are cooled. From the products of combustion in the inner zone, the temperature of the latter may be directly estimated using the reaction isochores of the equilibrium.

Habeshaw, J. *See* abs. 259.

1300. Hackspill, L. [Industrial Progress in the Use of High Pressures.] Chim. et ind., vol. 53, 1945, pp. 387–392; Chem. Abs., vol. 40, 1946, p. 5856.

Discusses the synthesis of NH_3 by the Haber, Claude, and Casale processes; the superpressures of Basset and their application in the synthesis of NH_3 without a catalyst; and the synthesis of MeOH, of Synthol, and the Bergius hydrogenation process.

1301. Haehnel, G. [Hydrogenation—a Further Development of High-Pressure Technique of the Ammonia and Methanol Syntheses.] Chem. Tech., vol. 2, 1950, pp. 83–87; Chem. Abs., vol. 44, 1950, p. 7040.

Discusses technology of the hydrogenation of coal to gasoline and diesel oil with the high-pressure techniques developed for the syntheses of NH_3 and MeOH.

1302. Haensel, V. Kaiser Wilhelm Institut für Kohlenforschung, Mülheim. CIOS Rept. XXV–1, 1945, 16 pp.; PB 284; TOM Rept. 9; TOM Reel 197; TAC Rept. SnMC–3.

Contains information obtained in interviews with Drs. Pichler and Koch. The subject matter on Ru catalyst, medium pressure catalysts, synthesis with Fe catalysts, isosynthesis, and aromatization has already been reported in abs. 1303, and 701. The magnetic-chemical investigation of the Fe catalyst showed that higher carbides, such as Fe_2C, can be formed during the synthesis at 220°, but that they decompose between 300°–400°, leaving Fe_3C as the only stable component. It was found that the most active catalysts were those containing the most Fe_3C. When the catalyst is pretreated at about $^1/_{10}$ atm. absolute pressure, more Fe_3C is obtained than at atmospheric pressure. During the synthesis, the amount of Fe_3C decreases at the catalyst deteriorates, while the concentration of Fe_3O_4 increases. When an equilibrium mixture of Fe_3C and Fe_3O_4 appears to exist in the catalyst, there is no rapid drop in activity, but with a higher concentration of Fe_3C an initial decrease in activity is observed. An attempt was made to prepare the Fe_2C by reducing Fe oxide with H_2 and then passing CO over it and measuring the CO_2 formed. Then H_2 again was passed over the catalyst at higher temperatures, and the amount of CH_4 was determined. From the data it was concluded that Fe_2C was formed. However, magnetic measurements showed that Fe_3C also was present, thus indicating that, along with Fe_2C and Fe_3O, a third carbide must be present richer in C than Fe_2C. In other words, the Fe_3C crystallites must be embedded in a phase with C:Fe ratio exceeding 2:1. Additional Curie points were observed but not identified. At higher temperatures, Fe_3C becomes sintered, and care must be taken to maintain the temperature low enough to prevent it. Formation of Fe_3C does not occur if the fresh untreated catalyst is impregnated with water gas under pressure at 220°. Some Fe_2C can be obtained at 280° under such conditions, but the catalyst produced is not good.

1303. ———. New Version of Fischer-Tropsch Reaction Gives 90% Yields of Isoparaffins. Nat. Petrol. News, Tech. Sec., vol. 37, 1945, pp. R955–R956.

Report of the U. S. Technical Oil Mission giving details of a laboratory-scale investigation of a 1-step synthesis carried out at the Kaiser Wilhelm Institut für Kohlenforschung, Mulheim. The 1-step synthesis of isoparaffins by the Fischer-Tropsch process can be performed by first producing higher alcohols (primarily isobutanol), then dehydrating the alcohols, and finally hydrogenating the olefins to the corresponding isoparaffins. Synthesis gas for the reaction is preferably in the ratio of $1.2CO:1H_2$ instead of $1CO:2H_2$. The reaction is carried out at 450° and 300 atm. It does not take place at atmospheric pressure, but as the pressure is increased yields improve. Above 300 atm. O_2-containing compounds begin to be formed and in increasing quantities. The throughput is about 5–10 times higher than in the regular Fischer-Tropsch process. Over 90% of the C_4 and C_5 fractions in the products are isocompounds, as compared to 10–15% in the normal reaction using Co or Fe catalyst. The yield of product varies 60–120 gm. of C_4 fraction and higher; depending upon the catalyst, the yield of C_4 and higher fraction is 80 gm. per m.^{3} of gas; that of C_3H_8, 10 gm. The products are as follows: C_4H_{10} (90% isobutane), 60–70% by weight; C_5H_{12} (96–98% isopentane), 20–30%; C_6C_7 and C_8, small amounts. The C_6 fraction contains no neohexane, but primarily 2 and 3 methyl pentanes and no n-hexane. Some naphthenes have been found in the higher-boiling fraction. The yield of C_6–C_8 fraction is higher at the lower temperature. Some alcohols, amounting to less than 10% of the hydrocarbons, a small amount of MeOH, and a large amount of isobutanol also are formed. The end gas from the synthesis consists of; CO_2, 30; N_2, 20; CH_4, 10%; and the rest CO and H_2. Catalysts found suitable are mainly oxides of Zn, Al, and Th used alone or in combination. Details are given on the preparation of the catalysts.

1303a. ———. Catalytic Cracking of Pure Hydrocarbons. Advances in Catalysis, Academic Press, Inc., New York, vol. 3, 1951, pp. 179–197.

The discussion covers the cracking of compounds representative of different hydrocarbon classes, the mechanism of catalytic cracking and the nature of cracking catalysts. 20 refs. are listed.

———. *See* abs. 1327.

Haensel, V., and Jones; J. P. I. G. Farbenindustrie A.-G. Works at Leuna. XIV. Oxo Process. *See* abs. 1478.

Haensel, V., Jones, J. P., and Horne, W. A. I. G. Farbenindustrie A.-G. Works at Leuna. XV. Synol Process. *See* abs. 1479.

Haffner, A. E. *See* abs. 2445.

1304. Hagemann, A. Catalytic Hydrogenation by the Fischer-Tropsch Process. Engineering, vol. 146, 1938, p. 517.

Digest of paper appearing in the Frankfurter Zeitung, June 1938.

Hagen, H. *See* abs. 3185.

Hager, K. F. *See* abs. 2260.

1305. Hägg, G. X-Ray Studies on the "Nitrides" of Iron. Nature, vol. 121, 1928, pp. 826–827; Chem. Abs., vol. 22, 1928, p. 4056.

creased space-time yield or by the production of more valuable products as raw material for the chemical industry, and further applications must be found for the products.

1322. ———. Production of Oil From Coal by the Fischer-Tropsch Process. Jour. Junior Inst. Eng. (London), vol. 57, 1947, pp. 309–334; Chem. Abs., vol. 42, 1948, p. 2743.

Discussion of the history and the main steps of the process, reaction products, and costs.

1323. ———. Recent Research on the Fischer-Tropsch Synthesis. Ind. Chemist, 1949, pp. 163–173; Chim. et ind., vol. 60, No. 3, 1948, p. 69; Fuel Abs. 1949, No. 1080.

Paper presented to Congres de chimie industrielle, 21st Congress, Brussels, September 1948. The Co catalyst process, hitherto used commercially, gives a low space-time yield of products, unsuitable as a source of motor fuel. By using an Fe synthetic NH_3 catalyst at high space velocities and temperatures, it has been shown, in confirmation of American claims, that the space-time yield can be increased 15 times and primary products suitable for the production of good-quality motor fuel can be obtained as the major final product. The use of residual gas recirculation is an essential requirement for achieving the desired results. The Fe catalyst is shown to be particularly active when used as a fluidized powder, and this system would be applicable for large-scale operation. The normal type of Co catalyst is unsuitable for operation under conditions of high conversion at high gas-space velocities. The results of experiments with a Co catalyst at temperatures below the normal synthesis range and of a study of the behavior of alcohols in the presence of Co and Fe catalyst give a strong indication that formation of alcohols is an intermediate step in the synthesis of hydrocarbons by the Fischer-Tropsch process.

1324. ———. Hydrogenation and Fischer-Tropsch Processes. Jour. Inst. Fuel, vol. 23, 1950, pp. 148–151; Chem. Abs., vol. 44, 1950, p. 6101.

General review of the development of the 2 processes for the synthetic production of liquid fuels from coal. The review covers the commercial development, process technique, chemistry, reaction mechanism, and present economic status. It is pointed out that most of the more recent advances in the technique of the 2 processes are the result of American work. Most of the investigations being made by both Government and industry have greater efficiency of method and increased economy of operation in view.

1324a. ———. Fischer-Tropsch Process. Birmingham Univ. Chem. Eng., vol. 2, 1951, pp. 84–92.

Review of the process since its early days.

1325. ———. Synthetic Liquid Fuel. Chem. Age, vol. 64, 1951, pp. 385–386.

Summary of a paper presented at a meeting of the Royal Institute of Chemistry. Brief review of research work in British and American laboratories on the synthesis of liquid fuels.

———. *See* abs. 446, 447, 672, 673, 674, 675, 1131, 1131a, 1417.

1326. Hall, C. C., and Craxford, S. R. Additional Information Concerning the Fischer-Tropsch Process and Its Products. BIOS Final Rept. 1722, 1946, 178 pp.; PB 93,498.

Acount of further investigations into the operation and development of the Fischer-Tropsch process in Germany including, specifically, a considerable amount of cost information at the more efficient plants and many important details of plant operation and research developments. The important subjects discussed are: Production of synthesis gas and its purification; Co catalysts, their composition, preparation, costs, reduction, and regeneration; design of reaction vessels; synthesis at atmospheric and medium pressures, recovery of products and general costs; synthesis with Fe catalysts, its mechanism, gas recycle, liquid phase, and oil recirculation processes; primary products, fatty acids and alcohols, Diesel oil, waxes, refining of primary products, analysis; Oxo synthesis; synthetic fatty acids and detergents, wax oxidation, synthetic soap and edible fats.

1326a. Hall, C. C., and Crumley, P. Observations on Fluidization as Applied to Fischer-Tropsch Process. Conf. Fluidization Technol., June, 1952; Jour. Appl. Chem. (U. S. S. R.), vol. 2, 1952, Suppl. 1, pp. S47–S55; Fuel Abs., vol. 12, No. 3, 1952, abs. 2,600.

Fischer-Tropsch process has been studied in beds of fluidized Fe catalyst in baffled tubes of small diameter; various fluidization phenomena peculiar to such a system and/or to the Fischer-Tropsch process are reported. The presence of baffles does not affect the validity of the normally acceptable criteria of fluidization but tends to promote segregation of the particles by hindering solids circulation. By use of a mechanical stirrer, a turbulent fluid condition can be obtained at about ½ the linear gas velocity otherwise necessary. Fischer-Tropsch Fe catalysts suffer little mechanical attrition as a direct result of fluidization but C formation within the particles causes rapid disintegration and reduction in particle size. In the presence of small amounts of wax formed in the synthesis the resulting small particles form fragile agglomerates approximating in shape to true spheres and greater in size than the largest particles in the original catalyst. Under conditions which favor C formation, the catalyst in a synthesis reactor is composed of particles of a wide range of densities and sizes. In narrow baffled beds the particles become distributed at various levels in the bed such that the height of a particle above the gas inlet is proportional to the product of the particle density and the square of its effective diameter. The largest particles, therefore, are not necessarily found at the bottom of the bed, nor those of lowest density at the top. The advantages and limitations of the use of fluidized catalysts in the Fischer-Tropsch process are reviewed.

1327. Hall, C. C., and Haensel, V. Combined Intelligence Objectives Subcommittee. Fischer-Tropsch Plant of Ruhrchemie A.-G., Sterkrade-Holten. British Coal Utilisation and Research Assoc., Monthly Bull., vol. 10, 1946, Abs. 1155; CIOS Rept. XXVII–69, 97 pp., PB 415, 1945; TOM Rept. 44; TOM Reel 197; TAC Rept. SnMC–11.

During the war the Fischer-Tropsch process was developed as the starting point for numerous processes yielding chemicals rather than fuels. Besides giving a detailed description of the synthesis-gas manufacture and the catalyst chambers used in the normal and medium-pressure processes, this report deals with: (1) The manufacture and recovery of the Co catalyst; and (2) the chemical and economic aspects of the Oxo process in which C_{12}–C_{18} alcohols are formed by hydrogenation of aldehydes produced by the reaction of olefins and synthesis gas over a Co catalyst. Reaction (2) also was studied in relation to a wide variety of other compounds, for example, cyclic olefins, styrene, butadiene, oleic alcohol, rubber, and vinyl ether. Costs are quoted as pf. 77 per kg. of alcohol. Much information was obtained on the manufacture of synthetic lubricating oils, the oxidation and chlorination of waxes, and the direct synthesis of higher alcohols and fatty acids.

1328. Hall, C. C., and Jolley, L. J. Fluidized-Solids Technique and Its Industrial Applications. Petroleum (London), vol. 13, 1950, pp. 217–223.

Summary of characteristics of fluidized-solid systems to indicate their advantages and limitations and to review their application to industrial processes, such as the refining of petroleum, Fischer-Tropsch process, manufacture of phthalic anhydride, burning of lime, carbonization and gasification of solid fuels, retorting of oil shale, hydrogenation of coal, and gas purification. Includes bibliography of 26 refs. and 8 flowsheets.

1329. Hall, C. C., and Powell, A. R. Krupp-Lurgi Low-Temperature Carbonization Plant. CIOS Rept. XXV–25, 1945, 8 pp., PB 288; TOM Reel 197; Iron and Coal Trades Rev., vol. 152, 1946, pp. 249–250.

Krupp works at Wanne-Eickel was primarily a Fischer-Tropsch plant for producing synthetic oil. In connection with it was a low-temperature carbonizing plant using high-volatile Ruhr coking coal to make a coke suitable for synthesis-gas production. The ovens were heated by the Fischer-Tropsch tail gas. The large coke was used in water-gas generators giving a water gas with a 1.35 ratio of H_2:CO, which is considerably higher than obtained from high-temperature coke. It was claimed that the process as carried out gave 30–35% more total oil than would be obtained from a high-temperature coking plant plus a Fischer-Tropsch plant.

1330. ———. Plant of Klocknerwerke A.-G., Castrop-Rauxel. CIOS Rept. XXV–7, 1945, 12 pp., PB 286; TOM Rept. 25; TAC Rept. SnMC–9; TOM Reel 197; British Coal Utilisation and Research Assoc., Monthly Bull., vol. 10, 1946, abs. 1046.

Synthesis gas consists of a 2:1 mixture of water gas and high-H_2-content coke-oven gas produced by thermal cracking. Operation of the cracking plant is described as well as the purification of the synthesis gas (0.25% O_2 is added for S removal). In the synthesis process the usual Co catalyst is regenerated with H_2 and by solvent extraction with Fischer-Tropsch benzine. Coke-oven gas also is separated into H_2, C_2H_4, etc. by partial liquefaction in 4 Claude plants and 1 Messer plant.

1331. Hall, C. C., and Smith, S. L. Life of a Cobalt Catalyst for the Synthesis of Hydrocarbons at Atmospheric Pressure. Jour. Soc. Chem. Ind., vol. 65, 1946, pp. 128–136. Chem. Abs., vol. 40, 1946, p. 5895.

Detailed account of the experimental operation of a Co–ThO_2–MgO–kieselguhr catalyst for the synthesis of hydrocarbons from CO and H_2 and the nature of the reaction products. The catalyst employed (Co 100, ThO_2 6, MgO 12, kieselguhr 200) was prepared by mixing simultaneously boiling solutions of Co and Th nitrates (40 gm. Co and 2.4 gm. ThO_2 per l. and Na_2CO_3 (88 gm. Na_2CO_3 per l.) and a warm, aqueous suspension of MgO and kieselguhr. After filtering, precipitating, washing, and drying, the catalyst was reduced by passing dry electrolytic H_2 downwards through it at a rate of approximately 560 l. per hr. for 2 hr. at 390°–405° and then cooling to 150°. Synthesis gas of composition CO_2, 2.5; CO, 31.4; H_2, 63.1; and N_2, 3.0% was passed through the catalyst at 150°, raised to 175° during 12 hr. and maintained for 24 hr., then raised to 180° for a second 24-hr. period and then to 185°, which was maintained constant. The synthesis gas rate was maintained at 1 l. per gm. Co per hr. throughout. Over a period of 14 months at atmospheric pressure an average yield of 122 gm. of liquid hydrocarbons per N $m.^3$ of inert-free synthesis gas was obtained. The composition of the liquid products remained unchanged throughout the period for a given reaction temperature. Increase in temperature caused an increase in the proportion of the gasoline fraction and a decrease in that of the wax fraction. Various methods of maintaining and restoring catalyst activity were examined, and it was concluded that maximum catalyst life is obtained by intermittent treatment with H_2 at temperatures in the synthesis range and by repetition of the original reduction process when a reaction temperature of 195° becomes necessary to maintain activity. By adhering to such a procedure it is estimated that with an active catalyst and a S-free gas (not more than 0.1 gm. S per 100 N $m.^3$) it should be possible to maintain in a single-stage synthesis an output of 115–120 gm. of liquid hydrocarbons per N $m.^3$ inert-free gas for 5–6 mo. without repetition of the reduction process and for at least 18 mo. before remanufacture of the catalyst becomes necessary. The experiments indicated the existence of 3 processes leading to the deterioration of the catalyst apart from S poisoning; the relatively rapid deposition on the catalyst of hydrocarbons readily removeable by the H_2 treatment; a change, possibly oxidation of the Co, which takes place more slowly and can be reversed by repetition of the original reduction procedure; and a still more gradual but more fundamental change, probably a physical alteration of the active surface of the catalyst or of the presence of some substance strongly absorbed on the active centers.

1332. ———. Hydrocarbon Synthesis in the Presence of Cobalt Catalysts at Medium Pressures. Jour. Inst. Petrol., vol. 33, 1947, pp. 439–459; Chem. Abs., vol. 42, 1948, p. 735.

Effect of a pressure of 150 p.s.i. on the synthesis of hydrocarbons from H_2 and CO with a Co:ThO_2:MgO:kieselguhr catalyst was studied. Conversion with synthesis gas (H_2:CO=2:1) was about 10% greater, and the rate of catalyst deterioration was 30–50% less than at atmospheric pressure. Improvement in performance over that at atmospheric pressure was not as marked as Fischer and Pichler obtained with their Co:ThO_2:kieselguhr catalyst. abs. 1011. Treatment with H_2 at synthesis temperatures did not lengthen the life of the catalyst; rereduction treatment at higher temperatures did not bring improvement under medium-pressure conditions. Catalyst with a high Co content per unit of volume produced an excessive amount of gaseous hydrocarbons at 150 p.s.i. This was corrected by using water gas (H_2:CO=1.2:1) instead of the synthesis gas. Gas production was reduced from 45 to 17 gm. per $m.^3$ of inert free charge, and at the same time, the production of nongaseous hydrocarbons was reduced only from 134 to 130 gm. per $m.^3$ of charge. The olefin content of the fraction b. 30°–150° was increased by the reduction of H_2 in the charge 8–53%. The highest conversion to liquid and solid hydrocarbons was obtained with a H_2:CO ratio of 1.5:1. In the first few weeks of the catalyst's life the conversion was 85% of the charge.

1333. Hall, C. C., and Taylor, A. H. Chemical Engineering Aspects of the Fischer-Tropsch Process. Trans. Inst. Chem. Eng. (London), Advance Copy, Jan. 7, 1947, 15 pp.; Ind. Chemist, 1947, pp. 231–239; Chem. Abs., vol. 41, 1947, p. 1827.

Summary of chemical engineering data on the Fischer-Tropsch process as collected in Germany by Allied investigators. Synthesis gas was produced from coke in standard water-gas generators, the ratio of H_2:CO being boosted from approximately 1.25:1 to the desired 2:1 with additional H_2 from coke-oven gas or by bringing a portion of the water gas into contact with a promoted Fe oxide shift catalyst. H_2S was removed from the gas by the ordinary Fe oxide process. Organic S compounds were removed by a novel hot-purification process in which the gas at 300° passed through towers containing granules of 70% Luxmasse and 30% Na_2CO_3. The O_2 (0.2%) in the inlet gas combined with the decomposition products of the organic S to deposit Na_2SO_4 on the granules. A drawing of the arrangement of equipment is shown. Synthesis was carried out at either atmospheric pressure or medium pressure (10 atm.). Separate systems were used for the 2 processes, and figures and tables are presented to give details of design, operation, efficiency, and costs of plants operating each process. Synthesis catalyst was granular (1–3 mm. in diameter), containing in parts, by weight: Co 100, ThO_2 5, MgO 8, kieselguhr 200. The reaction was exothermic (80 B. t. u. per cu. ft. CO and H_2 converted) and was carried out at a temperature of 170°–220°, depending on catalyst age. Approximately 80% of the reaction heat was recovered as steam generated in the cooling-water tubes running through the reaction zone. 2 reaction stages were used in the atmospheric-pressure process and 3 in the medium-pressure process. Catalyst in the 1st stage became coated with wax in 1–4 wk. and was solvent extracted with the 165°–320° cut of product to remove the wax. Primary products condensed and recovered included: (1) Liquefied C_3–C_4 gas, separated from other products by adsorption in active C and containing not more than 2% CO_2; (2) gasoline, b. 30°–165°. sp. gr. 0.68, Reid vapor point 0.5–0.8 atm., octane No. (motor) 45–52; (3) light Diesel oil, b. 165°–230°, sp. gr. 0.75, f. p. —40°, flash point 30°, cetane number 76, (4) gas gas oil, b. 230°–320°, used as raw material for detergent manufacture; (5) soft wax, b. 320°–460°, raw material for fatty acid synthesis; (6) hard wax, b. over 460°, m. 80°–90°, formed in the medium-pressure process only; and (7) catalyst wax, m. 80°–90°, recovered by solvent extraction of the catalyst. The chief obstruction to cost reductions in the German processes is the low space-time yield (maximum 0.2 ton primary product per cu. ft. reaction space per month, which is due to the necessity of having a large cooling surface for removing the heat of reaction. Alternate methods of cooling, which were in experimental stages, included gas recirculation or oil circulation, both through the catalyst space, with the heat being removed from the coolant outside the reaction zone. Mention is made of the recently developed American practice in which the use of the fluid catalyst technique has permitted a substantial increase in space-time yield.

1334. HALL, C. C., CRAXFORD, S. R., AND GALL, D. Interrogation of Dr. Otto Roelen of Ruhrchemie A.-G. BIOS Final Rept. 447, 1945, 50 pp.; PB 77,705; TOM Reel 226.

Discussion of Co catalyst, normal and medium-pressure synthesis, primary and secondary products, Fe catalyst, liquid-phase synthesis, incorporation of C_2H_2 in the synthesis gas, reaction mechanism in Fischer synthesis, the Oxo synthesis, and development of Co–ThO_2–MgO catalyst.

1335. ———. Interrogation of Dr. Otto Roelen of Ruhrchemie A.-G. The Catalyst. BIOS Final Report 447, 1945, pp. 2–9; An Account of the Development of Co–ThO_2–MgO Catalyst, by Dr. O. Roelen. Appendix III, pp. 48–52; PB 77,705; TOM Reel 226.

Original Fischer-Tropsch catalyst, Co 100 : ThO_2 18 : kieselguhr 100, was found to be slightly less active than one of composition Co 100 : ThO_2 15 : kieselguhr 100. This latter, however, had a short life (probably because of its high wax production) and a high CH_4 production owing to its high Co density. Therefore, the kieselguhr content was increased to about 200 parts, and a constant Co density of about 80 gm. per l. of catalyst was established. This appeared to be the minimum Co density allowable, since it is one of the main factors controlling the reducibility of the catalyst. In the search for a catalyst promoter, ThO_2 had been chosen as having satisfactory properties. It increased the activity, directed the synthesis to the production of the higher molecular-weight hydrocarbons, was easy to regenerate, was not sensitive to the influence of impurities, and reduced the thixothropic tendency of the wet catalyst filter cake to liquefy and destroy the essential colloidal structure. Cu was tested as an additive because of the possibility of reducing the catalyst at a low temperature but was at once ruled out owing to its favoring sintering of the finely divided Co and thus reducing the active life of the catalyst; it also favors the rapid saturation of the catalyst with wax. Mn was then tried and showed an effect similar to ThO_2, but its use was avoided because of the difficulties involved in the regeneration of the Co solutions. Systematic investigation of MgO showed that it was one of the best activators available for Co catalysts and combined with ThO_2 produced a synergistic effect, which made the mixed Co–ThO_2–MgO–kieselguhr catalyst the best thus far produced. Although Co–MgO catalysts are in themselves very sensitive to temperature and difficult to control, those containing both ThO_2 and MgO have the advantages of easier running, higher activity, easier regeneration, cheaper production, less subject to disintegration, and a well-balanced product. MgO directs the synthesis toward the formation of lighter products, and ThO_2 directs it toward higher molecular hydrocarbons and waxes, thus giving a product having a boiling range intermediate between the 2. The amount of ThO_2 can be reduced to as low as 5 parts giving a composition 100 Co : 5 ThO_2 : 8 MgO : 180–200 kieselguhr. The limits defining the best ratios of the 4 constituents are not narrow, so that variations in composition of catalysts prepared on a large scale are virtually of no importance. Kieselguhr as catalyst support was found to be the most suitable material investigated. In reducing the catalyst with H_2 it was found that the most active catalysts were obtained by stopping the reduction before all the Co was reduced to metal; the most active catalysts had reduction values of 65–70%. It was thought that the unreduced CoO may have a very important role in preventing sintering and, alternatively, that it may be a promoter for the synthesis itself. It was the opinion that further improvements in Co catalysts would not be from the standpoint of yield but rather in the direction of catalysts favoring the production of special types of products. Further investigations of CO–Mn–kieselguhr catalysts, which had a high activity at low temperatures (165°), with or without ThO_2, might be profitable.

1335a. HALL, C. C., GALL, D., AND SMITH, S. L. Alternative Techniques in the Fischer-Tropsch Synthesis. Fuel Abs., 1952, abs. 488; Fuel, vol. 31, 1952, p. 370.

Compares the fixed bed, the liquid phase (slurry) and the fluidized bed techniques. In the work carried out by the British Fuel Research Station on the 3 different techniques identical conditions of catalyst, temperature, pressure, gas composition and throughput, and recycle ratio have been maintained. The limitations of the fluidized bed system imposed a restriction as regards operating conditions with the other 2 techniques. For example the use of H_2–rich gas and temperatures of at least 300° was essential, as well as high fresh feed-gas rate. Experiments were made at both 300 and 600 p. s. i. g. Allowing for increase in activity with reduction in particle size of fused and sintered catalysts, activity of the catalyst is the same in the fixed- and fluid-bed systems, but appreciably lower in the liquid phase system. The space-time yield, which is dependent on catalyst concentration, is greatest in the fixed bed and lowest in the liquid phase. Fluidization itself does not increase the rate of reaction, but the presence of the liquid medium in the slurry process retards the reaction rate. Selectivity as judged by CH_4 formation expressed as a % of the total CO converted, is approximately the same in the fixed and fluid beds but appreciably higher in the slurry system. This is attributed to the prevention of localized high temperatures because of the direct contact between catalyst particles and liquid medium. The boiling range and olefin contents of the liquid products are independent of the nature of the process technique, as also is the formation of C with a given catalyst.

1336. HALL, C. C., CRAXFORD, S. R., GALL, D., AND SMITH, S. L. Medium-Pressure Synthesis With Iron Fixed-Bed Catalysts and Operation of the Fischer-Tropsch Synthesis in the Liquid Phase—Interrogation of Dr. H. Kölbel, Rheinpreussen. BIOS Final Rept. 1712 (Interrogation Rept. 679), December 1947, 7 pp.; PB 91,925.

Good catalyst composition was found to be, in parts by weight: Al_2O_3, 3.4; Fe_2O_3, 46.3; CaO, 40.7; MgO, 6.5; CuO, 3.1; K_2O, 0.5; CO_2, 40.1; the main constituents being Fe and dolomite. The catalyst was prepared by precipitation from the nitrates by Na_2CO_3 solution. The critical step was the pretreatment in synthesis gas at 240°–280° at atm. pressure for 3–24 hr. The gas was recirculated in the proportion of 9 parts of recycle gas to 1 of fresh gas at a minimum space velocity of 1,000 vol. per vol. catalyst per hr. After cooling the catalyst, synthesis is started at 10 atm. and the full space velocity (100–150), the temperature varying from catalyst to catalyst. Multistage operation is preferred, with recirculation of the residual gas. With 3 stages, a Co-conversion of 90–95% can be obtained at an over-all space velocity of 150. Investigation of operation in the liquid phase with the catalyst suspended in oil of Diesel oil composition was carried out over several years with favorable results. The usual catalyst composition was Fe, 100; Cu, 0.2; K_2CO_3, 1.0. Some performance data are given. Using a benzine-forming catalyst at 8–10 atm., 230°, and a space velocity of 75 vol. gas per vol. reaction space per hr., the synthesis gas has a H_2 : CO ratio of 0.5 : 1, and a total yield of 168 gm. per m^3 was obtained with a utilization ratio of H_2 : CO=0.5 : 1. No CH_4 was detected, and the amount of C_2H_6 was very small. Distribution of the product was: C_3–C_4, 19.6%; 35°–200°, 55%; 200°–320°, 20.8%; 320°, 5.6%. The fraction 35°–150° contained 60% olefins. Using catalysts that tended to produce wax, as much as 67% of the total product was obtained as such. It was observed that the Diesel oil used as the liquid medium took part in the reaction and was converted to wax.

1337. HALL, C. C., and others. Coal, Shale, Peat, and Their Products. I. Fuels Produced by Hydrogenation and Synthetic Processes. Rev. Petrol. Technol., vol. 10, 1948, pp. 244–263.

1338. HALL, G. H. Labour's Plan for Oil From Coal. Labour's Pub. Dept., London, 1938, 79 pp.

See Egloff, abs. 771.

HALL, W. K. *See* abs. 41, 45, 47, 48, 50, 54, 2073a, 2228.

HALL, W. K., TARN, W. H., AND ANDERSON, R. B. Studies of the Fischer-Tropsch Synthesis. VIII. Surface-Area and Pore-Volume Studies of Iron Catalysts. *See* abs. 51.

HALL, W. K., TARN, W. H., AND ANDERSON, R. B. Studies of the Fischer-Tropsch Synthesis. XIII. Structural Changes of a Reduced Iron Catalyst on Reoxidation and on Formation of Interstitial Phases. *See* abs. 53c.

1339. HALLS, E. E. Synthetic Waxes. Food, vol. 19, 1950, pp. 27–28, 68–70, 108–110; Chem. Zentralb., 1950, II, p. 595.

Survey of synthetic waxes, including those from the Fischer-Tropsch process, their production, properties, and uses.

1339a. HALSEY, G., AND TAYLOR, H. S. Adsorption of Hydrogen on Tungsten Powders. Jour. Chem. Phys., vol. 15, 1947, pp. 624–630; Chem. Abs., vol. 41, 1947, p. 7,200.

Frankenburg's data (abs. 1081a) on the adsorption of H_2 by W powder from —194°–750° are analyzed by the Fowler-Guggenheim treatment.

1340. HALSEY, G. D. Physical adsorption on Nonuniform Surfaces. Jour. Chem. Phys., vol. 16, 1948, pp. 931–937; Chem. Abs., vol. 42, 1948, p. 8,573.

Analysis of adsorption on a uniform surface by using the quasichemical theory of interaction shows that the hypotheses of the Brunauer-Emmett-Teller theory lead to substantially no adsorption beyond the first layer if $E_2=E_L$, and stepwise isotherms if $E_1>E_2>E_3 \cdots >E_L$. For the monolayer adsorption of gases on Ag, Pt, and steel, the heterogeneous nature of the adsorbing surface is clearly indicated. Cooperative adsorption on the nonuniform surface is treated and the cooperative analog of the Freundlich equation derived. The typical multilayer isotherm is shown to be composed of 3 regions: Noncooperative adsorption on a strongly heterogeneous surface; cooperative adsorption on a still heterogeneous surface: and cooperative multilayer adsorption induced by small van der Waals perturbations some distance from the surface. The isotherm p/p_0=experiment $(-a/O^r)$ is derived and shown to be a good representation of adsorption data that conform to the Brunauer-Emmett-Teller type I, II, or III shapes.

1341. ———. Rate of Adsorption on a Nonuniform Surface. Jour. Phys. Colloid Chem., vol. 55, 1951, pp. 21–26; Chem. Abs., vol. 45, 1951, p. 3,220.

On the assumption that the activation energy for the adsorption process is proportional to the zero-point energy between the gas and the solid, an expression is derived for the rate of adsorption of a gas on a nonuniform surface, and it is shown that it is in qualitative agreement with earlier observations of the adsorption of H_2 on ZnO.

1342. HAMAI, S. Physicochemical Investigations of Catalytic Mechanisms. I. Fischer-Tropsch Synthesis of Hydrocarbons With Special Reference to Its Mechanisms. Jour. Chem. Soc. Japan, vol. 62, 1941, pp. 516–518; Chem. Abs., vol. 37, 1943, p. 4681.

In the Fischer-Tropsch synthesis of hydrocarbons the catalyst acts as a carrier, as ascertained in 350 experiments. With Co the catalytic mechanism is as follows: Co adsorbs CO on its surface, and the CO is hydrogenated to CHOH. CoCHOH by catalytic reduction is changed into $CoCH_2$ and H_2O. In the beginning when the amount of $CoCH_2$ is small as compared with that of H_2, CH_4 is formed by the reaction $CO+3\ H_2 \rightleftharpoons CH_4+H_2O$ (particularly when CO : H_2 is greater than 1 : 3) or at 300° CH_4 results from the reaction $CoCH_2+H_2 \rightleftharpoons CH_4+Co$. However, at the later stage of the reaction or at 200° CH_4 is not formed. The $CoCH_2$ then polymerizes into $Co(CH_2)_n$, which further separates into Co and $(CH_2)_n$, the hydrogenation of the latter resulting in a high hydrocarbon (liquid). This catalytic mechanism was found with Fe and Ni. In the case of Fe (synthesis carried out at 250°), however, CO_2, instead of H_2O, was obtained after the catalytic reduction owing to the presence of the rapid reaction $CO+H_2O \rightleftharpoons H_2+CO_2$.

1343. ———. Physicochemical investigations of Catalytic Mechanism. II. Fischer-Tropsch Synthesis of Hydrocarbons With Special Reference to Its Reaction Mechanisms. Bull. Chem. Soc. Japan, vol. 16, 1941, pp. 213–228; Chem. Abs., vol. 36, 1942, p. 739.

Following mechanism of the Fischer-Tropsch synthesis over a Co catalyst is proposed and discussed from the standpoint of energetics and thermodynamics: CO is adsorbed or displaces H_2 adsorbed on the Co surface, forming $Co{-}Co({-}C{=}O)Co$, which is reduced first by adsorbed H_2 to $Co{-}Co({-}HCOH)Co$, then to $Co{-}Co({-}CH_2)Co$. The (CH_2) mol. adsorbed on the Co surface migrate freely over the surface to interact with one another to form Co—Co(—$CH_2CH_2CH_2CH_2$ . . . . . .)Co, which, upon desorption, yields $(CH_2)_n$ and finally liquid products by hydrogenation. At 200°, Co—Co(—C=O)Co does not form CH_4 by hydrogenation, but at 300° CH_4 is formed: CH_4 formation probably results from reaction of CO and H_2 in the gas phase. Maximum adsorption does not necessarily coincide with maximum catalytic activity. The same mechanism applies to Fe- and Ni-type catalysts. If the catalyst is pretreated with CO at 350°, it suffers a loss of activity, possibly owing to prevention of adsorption of H_2 by the adsorbed CO.

1344. Hamai, S., Hayashi, S., and Shimamura, K. Physicochemical Investigation of Catalytic Mechanisms. III. Desorption of Various Gases From the Catalyst Used in the Fischer-Tropsch Synthesis. Jour. Soc. Chem. Ind. Japan, vol. 45, 1942, pp. 313–318; Chem. Abs., vol. 43, 1949, p. 2401.

To study the mechanism of catalysis in the synthesis of hydrocarbons from CO and H_2, a Co catalyst with certain promoters was heated 190°–200° and saturated with H_2, CO, or N_2. Another 1 of the 3 gases was then passed over the catalyst, and the velocity of desorption of the original gas was measured by analysis of the exhaust gas. H_2 was more quickly desorbed than CO. A comparison of the desorption of CO by H_2 and of H_2 by CO indicates that CH_4 formation predominates when there is an excess of H_2. The mechanism of the Fischer-Tropsch reaction is proposed to be $Co_nCO \rightarrow Co_nCHOH \rightarrow Co_nCH_2$.

1345. Hamai, S., Hayashi, S., Shimamura, K., and Igarashi, H. Physicochemical Investigations of Catalytic Mechanisms. IV. Fischer-Tropsch Synthesis of Hydrocarbons. Experiment Series 1. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 166–171; Chem. Abs., vol. 41, 1947, p. 4366.

Experiments substantiated the authors' proposed mechanism for Fischer-Tropsch synthesis. The reaction vessel of Terex glass was made double walled so that the gas mixture, $CO+2H_2$, led in could be heated before entering the catalyst zone. The catalyst used was made of Co, CeO_2, ThO_2, B_2O_3, and diatomaceous earth. The reaction was run at 200° at the rate of flow 4 l. per hr. The reaction products were collected in 2 traps, condensed by water and solids $CO_2—C_2H_5OH$ mixture, respectively. The gas contraction and oil yield were not parallel unless the reaction was normalized. In the initial stage CH_4 formation predominated, cutting down the oil formation, but as time proceeded side reactions other than oil formation were inhibited. Physicochemical properties of the reaction products are tabulated. The catalyst used proved to be very durable.

1346. Hamai, S., Hayashi, S., and Shimamura. K. Physicochemical Investigations of Catalytic Mechanisms. V. Fischer-Tropsch Synthesis of Hydrocarbons. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 252–259; Chem. Abs., vol. 41, 1947, p. 4367.

Co with kieselguhr was used as catalyst with various amounts of ThO_2, CeO_2, and Cu as promoters. Gas contraction and oil formation from CO and H_2 are recorded. The gas contraction % is higher for 15–10% CeO_2 and for 20–30% ThO_2. When CeO_2% is low, the addition to the ThO_2 lowers the activity, but if CeO_2 is high, the addition of ThO_2 does not improve the gas contraction. CeO_2 gives a relatively high yield of oil and low yield of CH_4, whereas ThO_2 gives a relatively high yield of CH_4 and low yield of oil.

1347. Hamai, S. Physicochemical Investigations of Catalytic Mechanisms. VI. Fischer-Tropsch Synthesis of Hydrocarbons. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 339–344; Chem. Abs., vol. 41, 1947, p. 4367.

Effects of B_2O_3 in the Co-type catalysts are reported. When CH_4 formation predominates the contraction % is enormously high, and the oil yield is inappreciable.

1348. ———. Physicochemical Investigations of Catalytic Mechanisms. VII. Durability and Pretreatment of the Catalyst Used for the Fischer-Tropsch Synthesis of Hydrocarbons. Jour. Chem. Soc. Japan, vol. 63, 1942, pp. 1606–1615; Chem. Abs., vol. 41, 1947, p. 3273.

Catalyst used in the Fischer-Tropsch synthesis of hydrocarbons can be revivified by reducing with H_2.

1349. Hamai, S., Hayashi, S., and Shimamura, K. Physicochemical Investigations of Catalytic Mechanisms. VIII. Fischer-Tropsch Synthesis of Hydrocarbons With Special Reference to the Durability of Catalyst. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 451–461; Chem. Abs., vol. 41, 1947, p. 4367.

Reaction (I), $CH_2 \rightarrow C_2H_4$, is faster than (II), $CH_2 \rightarrow CH_4$. In the normalized reaction (I) is predominant under various conditions of stage of reaction, temperature, etc., whereas (II) is predominant at the initial stage and as the reaction becomes normalized. (II) must be prohibited when the reaction mixture, $CO+H_2=(1:2)$, is passed through the catalysts, Co+15% ThO_2+100% kieselguhr or Co+12% U_3O_8+2.8% Cu+100% kieselguhr, each separately at 190°–250°.

1350. ———. Physicochemical Investigations of Catalytic Mechanisms. IX. Fischer-Tropsch Synthesis of Hydrocarbons, With Special Reference to Factors Essential to the Particular Catalysts. Bull. Chem. Soc. Japan. vol. 17, 1942, pp. 463–477; Chem. Abs., vol. 41, 1947, p. 4367.

Effects of the factors are tabulated, including the composition of the catalysts (Co, U_3O_8, Cu, Mn, and kieselguhr), preactivation temperature, and reaction temperature for the reaction mixture of $CO+H_2$. The presence of kieselguhr contributes to the oil formation, but not the CH_4 formation. Generally higher temperature promotes the formation of gaseous products, such as CH_4 and CO_2, and a very small amount of oil formation.

1351. Hamai, S. Physicochemical Investigations of Catalytic Mechanisms. X. Reaction Products in the Fischer-Tropsch Synthesis. Experiment Series 2. Bull. Chem. Soc. Japan, vol. 18, 1943, pp. 369–375; Chem. Abs., vol. 41, 1947, p. 4367.

Results of the distillation analysis of the products show that the first trap oil contains $C_{12}–C_{13}$ and the second trap oil contains $C_7–C_9$ predominantly, as compared with other fractions.

Hamai, S. Physicochemical Investigations of Catalytic Mechanisms. VI. Fischer-Tropsch Synthesis of Hydrocarbons. *See* abs. 1347.

———. Physicochemical Investigations of Catalytic Mechanisms. VII. Durability and Pretreatment of the Catalyst Used for the Fisher-Tropsch Synthesis of Hydrocarbons. *See* abs. 1348.

———. Physicochemical Investigations of Catalytic Mechanisms. X. Reaction Products in the Fischer-Tropsch Synthesis. Experiment Series 2. *See* abs. 1351.

Hamai, S., Hayashi, S., and Shimamura, K. Physicochemical Investigation of Catalytic Mechanisms. III. Desorption of Various Gases From the Catalyst Used in the Fischer-Tropsch Synthesis. *See* abs. 1344.

———. Physicochemical Investigations of Catalytic Mechanisms. V. Fischer-Tropsch Synthesis of Hydrocarbons. *See* abs. 1346.

———. Physicochemical Investigations of Catalytic Mechanics. VIII. Fischer-Tropsch Synthesis of Hydrocarbons With Special Reference to the Durability of Catalyst. *See* abs. 1349.

———. Physicochemical Investigations of Catalytic Mechanisms. IX. Fischer-Tropsch Synthesis of Hydrocarbons With Special Reference to Factors Essential to the Particular Catalysts. *See* abs. 1350.

Hamai, S., Hayashi, S., Shimamura, K., and Igarashi, H. Physicochemical Investigations of Catalytic Mechanisms. IV. Fischer-Tropsch Synthesis of Hydrocarbons. *See* abs. 1345.

1352. Hammerich, T. Analytical-Arithmetical Way of Finding the Research Octane Number in Gasoline of the Fischer-Tropsch Synthesis. FIAT Reel K–25, 1940, frames 3,853–3,889; PB 70,216; TOM Reel 292.

Gasolines of the Fischer synthesis were selected since they contain only straight chains of aliphatic hydrocarbons. From these gasolines the C_3 and C_4 hydrocarbons were separated. Density at 15° C., I number after the Rosenmund and Kuhnhenn method, and the distillation curve were determined for each gasoline. From a comparison of the olefin contents, I number, and boiling range, certain relations could be established, which were reproduced in a graph. By adding the gasifying property of gasoline new graphs could be drawn for direct octane-number reading.

1353. ———. [Analytical-Arithmetical Determination of the Research Octane Number of Gasolines From the Fischer-Tropsch Synthesis.] Oel u. Kohle, vol. 37, 1941, pp. 148–155; Brennstoff-Chem., vol. 22, 1941, p. 154; British Abs., 1948, B, I, p. 281; Chem. Abs., vol. 35, 1941, p. 8268.

For degasified Fischer-Tropsch gasolines, octane No.=0.7×0.4×(olefin index)+0.69×(vaporizability), the olefin index being equal to (I number×boiling index)/100, and vaporizability the mean of the constituents going over at 60° and at 100°. For 115 gasoline samples covering production of nearly all German plants, 60% showed 0 to ±1 deviation from the Cooperative Fuel Research octane No.; 20% showed ±1.5 deviation: 15% up to ±3 units; and the remaining 5% from ±3.5 to ±5. Mixed octane numbers in 1:1 mixture with Stanavo aviation gasoline, however, showed considerable deviation. The relationship is not valid if the synthesis conditions are changed or if the gasoline has been treated. Diagrams are given from which octane No. may be read directly.

1254. Händler, H. [Synthesis of Petroleum.] Allgem. österr. chem.- u. tech. Ztg., vol. 42, 1924. pp. 89–91; Chem. Abs., vol. 18, 1924, p. 2955.

General discussion of the possibility of making synthetic petroleum by hydrogenation of CO, CO_2, or coal.

1355. Hanemann, H. [Higher Eutectics in the Iron-Carbon Alloys.] Ztschr. anorg. Chem., vol. 84, 1914, pp. 1–23; Chem. Abs., vol. 8, 1914, p. 2142.

To check the results of Vittorf, pure Fe–C alloys were melted at temperatures observed with an optical pyrometer and poured into Fe chills. The cementite contents of the samples gave points on a curve agreeing with the results obtained by Vittorf and Ruff, but the accuracy of this determination decreases at high temperatures. Graphite always separates as a primary product from melts poured from above 1,400°. Vittorf's method of analyzing the crystals separating from the melts is criticized, owing to the difficulty of getting a good separation because of the high viscosity of melts made between 1,700° and 2,500°. At 2,500°, quenched specimens gave an analysis 14% of C, mostly as enmeshed graphite. Ruff's conclusion that the solubility of C decreases at very high temperatures was not confirmed. Vittorf's Fe_4C is believed to be austenite, as it goes over to martensite upon quenching in liquid air, and his FeC and FeC_2 are believed to be graphite.

———. *See* abs. 1170.

1356. Hanemann, H., Herrmann, K., Hofmann, U., and Schrader, A. [Processes in the Formation of the Martensite Structure.] Arch. Eisenhüttenw., vol. 4, 1931, pp. 479–484; Chem. Abs., vol. 25, 1931, p. 4833.

Martensite system was studied by the most recent röntgenographic methods, and a correlation of the conclusion from recent Röntgen investigations with the facts of micrographs was attempted. The tetragonal, space-centered lattice of hardened steels with 0.91% C as determined by röntgenographs primarily is due to the η-phase. The röntgenographs of steel samples with higher C contents (1.64% C) contain, besides the interferences of the tetragonal lattice, those of cubic face-centered Fe (austenite). A distorted α–Fe lattice with the embedded and adsorbed C atoms exists between the first and second martensite transformations. The röntgenographs show the disappearance of the η–phase on annealing, hardened, high–C steels at 110°, while the photomicrographs show that the needle-formed η–structure is unchanged (a case of pseudomorphism). In photomicrographs the θ–phase is crystalline in form, while in the röntgenographs it shows a primary structure different from that of α–Fe (another case of pseudomorphism). On quenching steels with 0.91% C from 1,100° and 900° in ice–H_2O and from 900° in oil, the tetragonal structure remains unchanged within wide limits of quenching velocity.

Hara, I. *See* abs. 1905, 1906b.

1357. Hardy, D. V. N. Interaction of Olefins, Carbon Monoxide, and Steam. Jour. Chem. Soc., 1936, pp. 364–365; Chem. Abs., vol. 30, 1936, p. 3771.

Passage of a mixture of 1 volume C_2H_4 and 4 volumes CO under a pressure of 150 atm. at a rate of 40 l. compressed gas/hr. through 350 gm. 87% H_3PO_4 at 290°–300° gives 500 gm. product containing 16.5 gm. high-boiling hydrocarbons, 37 gm. EtOH, and a solution of Na salts containing $EtCO_2H$. For every molecule C_2H_4 converted into acid, approximately 3 were hydrated and 2 polymerized. C_3H_6 and CO at 200° and 200 atm. (850 gm. C_3H_6 during 6 hr.) give 546 gm. of an upper layer (41% free acid) and 284 gm. of a lower layer (6.2% free acid). After refluxing 2 hr. with NaOH there were isolated 88.4 gm. volatile and 61.3 gm. nonvolatile hydrocarbons, 3 gm. Me_2CHOH, 10.5 gm. acids, boiling 150°–159°, and 173 gm. residue. Me_2CHCO_2H was identified. Iso–C_4H_8 (640 gm.) gave 10.6 gm. hydrocarbons, 32.5 gm. acid, boiling 160°–168°, 23.1 gm. acid, boiling 168°–190°, and 24.2 gm. residue. Esterification gave 32.8% of Me pivalate and 22.6% $MeEtCHCO_2Me$. Homologs also were present but not identified.

———. *See* abs. 2318.

Hardy, R. L. *See* abs. 2459.

Harkness, R. W. *See* abs. 829, 830.

1358. Harkness, R. W., and Emmett, P. H. Conversion of Ortho to Para Hydrogen Over Promoted Iron Synthetic Ammonia Catalysts at —190°. Jour. Am. Chem. Soc., vol. 55, 1933, pp. 3496–3497; Chem. Abs., vol. 27, 1933, p. 4730.

Adsorption of H_2 by a promoted Fe synthetic NH_3 catalyst inhibits markedly the activity of the latter toward the *o*–*p*-conversion at —190°; the results indicate definitely that the activated adsorption of H_2 at the higher temperatures is primarily a surface adsorption and not a solution within the Fe sample. Permitting the promoted catalyst to take up O_2 between room temperature and 450° almost eliminates its high-temperature activity toward the *o*–*p*-conversion but only slightly impairs the activity toward the conversion at —190°.

1359. ———. Two Types of Activated Adsorption of Hydrogen on the Surface of a Promoted Iron Synthetic Ammonia Catalyst. Jour. Am. Chem. Soc., vol. 56, 1934, pp. 490–491; Chem. Abs., vol. 28, 1934, p. 1588.

There are 3 types of adsorption of H on a promoted Fe catalyst (1.3% Al_2O_3 and 1.59% K_2O): *Physical*, at —196°, —183°, and —144°, at which temperatures 10 cc. of catalyst adsorbs 5, 2.8, and 0.25 cc. H, respectively; *type A activated*, between —78° and 0°, the isobar at 760 mm. showing a gradual decrease from an adsorption of 7–8 to 5–6 cc.; *type B activated*, at 100° or higher, an additional but much slower adsorption, the total adsorption of both types reaching 8–9 cc. at 100° in 2 hr.; at 212° and 450° the adsorption reached an apparent equilibrium in less than 1 hr., the adsorption being 5.5 and 3.5 cc., respectively.

1360. Harman, R. W. Substitute Motor Fuels in Australia. Jour. Proc. Australian Chem. Inst., vol. 8, 1941, pp. 270–284; British Chem. Abs., 1943, B, I, p. 54.

Shale oil, benzol, and power alcohol can at present supply about ⅓ of Australia's consumption. Any large extension of power alcohol would have to use wheat as raw material. Cost of production is about 2 s. per gal. Greater possibilities are seen in the Fischer-Tropsch synthesis, which, however, is not yet in operation in Australia.

Harnisch, C. *See* abs. 2998.

1361. Harris, C. P. Liquid Fuels From Gas—Synthetic Gasoline From Water Gas. Oil Weekly, vol. 45, No. 8, 1927, pp. 31–32, 48; Am. Gas Jour., vol. 126, 1927, p. 566. Progress in Gas Tech., pp. 18, 20; Chem. Abs., vol. 21, 1927, p. 2785.

Brief review of research on the production of synthetic fuels from gases and coal.

Hartley, H. *See* abs. 1421, 1423.

1362. Hartner-Seberich, R., and Koch, H. [High-Boiling Oils (Kogasin II) Obtained in the Benzine Synthesis of Fischer-Tropsch as Fuel for Diesel Motor Operation.] Brennstoff-Chem., vol. 13, 1932, pp. 308–310; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 537–541: Chem. Abs., vol. 26, 1932, p. 5733.

Constitution, physical, and fuel properties of Kogasin II were investigated. Distillation curves and behavior in motor tests are similar and equal to those obtained with a gas oil.

1363. Hasche, R. L., and Boundy, R. H. Inspection of the Oxo Plant at Ruhrchemie A.-G., Oberhausen-Holten. CIOS Rept. XXVII–18, 1945, 4 pp.; PB 390; TOM Reel 197.

This plant is owned jointly by the Ruhrchemie A.-G., the I. G. Farbenindustrie A.-G., and Henkel & Co. It is damaged very little and could produce 10,000 tons per year of products within 3 mo. Olefins of the C_{11}–C_{17} fraction, obtained by cracking in a Dubbs-type furnace of a C_{20}–C_{40} Fischer-Tropsch fraction, are treated with water gas in the liquid phase at approximately 150 atm. to produce a mixture of straight-chain aliphatic aldehydes and ketones, the former of which are reduced to the corresponding alcohols. Yields of olefins of approximately 50% are obtained in the cracking unit at 400°–450°. The converter is charged with a 50% suspension of the catalyst (90% Co, 7% ThO_2, 3% MgO, deposited as carbonates on kieselguhr) in the liquid olefins, and water gas is admitted at the bottom at 150 atm. pressure. Temperatures range 150°–180°, the higher temperature favoring aldehyde production but reducing the yield owing to polymerization. The yield of alcohols is approximately 1 lb. per lb. of olefins. The process may be carried out with C_2H_4 for production of lower aldehydes, particularly propionaldehyde, at temperatures of 85° and 70% yield. The catalyst can be used 50–100 times without regeneration. The oxygenated compounds are separated from the unreacted olefins by fractional distillation.

Hashimoto, G. *See* abs. 1930.

1364. Haskell, G. Research Plans in Synthesis Process of the United States Industrial Chemicals, Inc. Oil Gas Jour., vol. 46, No. 37, 1948, p. 111.

U. S. Industrial Chemicals, Inc., is cooperating with Stanolind Oil & Gas Co. in investigating the separation and use of chemical products from the hydrocarbon synthesis process. The processing materials will be obtained from the 2 hydrocarbon-synthesis plants now under construction by the Carthage Hydrocol, Inc., at Brownsville, Tex., and for the Stanolind Oil & Gas Co. at Hugoton, Kans.; and from the 2 auxiliary chemical plants projected by the latter. In a plant of its own the U. S. Industrial Chemicals, Inc., will process the primary chemicals from the auxiliary chemical plants. The process will involve the breaking down of the water-soluble chemicals to yield initially upwards of 300 million lb. per yr. of chemicals including solvents, plasticizers, pharmaceuticals, plastics, etc., at prices competitive with those from other sources.

1365. Haslam, R. T., and Forrest, H. O. Methane by Catalysis From Carbon Monoxide in Blue Water Gas. Gas Age-Record, vol. 52, 1923, pp. 615–618, 620; Chem. Abs., vol. 18, 1924, p. 321.

When the H_2 and CO of blue water gas in the approximate ratio of 1 : 1 interact at a temperature of 290°–340° with Ni as a catalyst the main reaction is: $2\,CO+2\,H_2=CH_4+CO_2+59.300$ calories. Approximately ⅕ of the CO present reacts according to $CO+3\,H_2=CH_4+H_2O+48{,}900$ calories. With reduced Ni as a catalyst the optimum conditions for the conversion of blue gas to CH_4 at atmospheric pressure is a time of contact of 10 sec. at a temperature 300°–330°. Under these conditions, the gas with a gross heating value of 520 B. t. u. per cu. ft. at 0° has the composition: CH_4, 47%; H_2, 5; CO_2, 44; N_2, 4. Increasing the pressure up to 35 p. s. i. has little effect on the ultimate composition of the gas except to require a slightly higher temperature for a given product. At the above temperature range, the energy lost in the conversion amounts to 20% of the total input. At this temperature there appears to be no C deposition on the catalyst. The impurities present in the cooled water gas have little effect on the vigor of the catalyst. This process has an efficiency of carburetion when producing 520 B. t. u. gas of 61.8%; this can be increased to 80% by washing out the CO_2 under pressure, thus raising the heating value to 834 B. t. u. With coke at $9.00 per ton the material cost of the process will be equal to the material cost of oil carburetion when gas oil costs $0.07 per gal.

1366. Haslam, R. T., and Thiele, E. W. Progress in Fuels and Fuel Technology. Ind. Eng. Chem., vol. 16, 1924, pp. 749–753; Chem. Abs., vol. 18, 1924, p. 2591.

Brief review of research and development in the field of fuels and combustion. Mentions Bergius and the Synthol processes.

Hassid, N. *See* abs. 2213b.

1367. Hatzfeld, K. Coal processing in Germany. Bergbau, Jan. 7, 1937, pp. 2–10; Coal Carbonisation, vol. 3, 1937, p. 46.

Processing of coal as related to the 4-Year Plan is discussed. Low-, medium- and high-temperature carbonization, coal gasification, high-pressure hydrogenation, Fischer-Tropsch synthesis, coal dust engines, and colloidal fuel are reviewed. The manufacture of gasoline by coal hydrogenation will provide employment for 8,000 miners per million ton of gasoline produced, each ton needing 3.5 tons of coal. About 650,000 tons of gasoline by the I. G. Farbenindustrie A.-G. process and 150,000 tons by the Fischer-Tropsch process are already being produced in German plants. The capital cost of the Fischer-Tropsch plant is about one-half that of the I. G. Farbenindustrie A.-G. plant and has the advantage of using coke, 6–7 tons being required per ton of kogasin. The Pott-Broche extraction process is in use at the Mathias Stinnes mine. More than 85% of the coal substance is brought into solution. The Uhde process is under development in the Ruhr district. By these various means Germany will soon be independent of imported gasoline and light oils.

1368. Haul, R., and Schoon, T. [Elementary Range of Ferromagnetism.] Ztschr. Elektrochem., vol. 45, 1939, pp. 663–671; Chem. Abs., vol. 34, 1940, p. 298.

γ–Fe_2O_3 was prepared by oxidation of Fe pentacarbonyl. The magnitude of the primary crystals decreases with decreasing reaction temperature until finally preparations are obtained amorphous to X-ray. When crystal identification by means of X-ray is no longer possible, electron rays are used. The magnetic susceptibility is measured by the cylinder method with different field strengths. Up to a range of lattice magnitudes of about 30–40 Å., there is a slight increase in susceptibility, which then rises about 10% to the amount characteristic of ferromagnetic substances. This experimentally determined value marks the lowest elementary particle at which spontaneous magnetization occurs.

1369. ———. [Structure of Ferromagnetic Ferric Oxides; γ–Fe_2O_3.] Ztschr. physik. Chem., vol. B–44, 1939, pp. 216–226; Chem. Abs., vol. 34, 1940, p. 666.

X-ray studies of γ–Fe_2O_3 prepared from Fe_3O_4, from an Fe arc, and from $Fe(CO)_5$ resulted in the values, $a_w=8.316\pm0.004$, 8.333 ± 0.004 and 8.3Å., respectively. No essential difference was found in lattice constant or intensity distribution in the 3 samples. Both X-ray and electron-diffraction powder diagrams showed new interference patterns. They can be explained on the assumption of lower symmetry or a larger elementary cell. Similar results were found in Al_2O_3.

Hawk, C. O. *See* abs. 3210, 3214, 3215, 3297.

1370. Hawk, C. O., Golden, P. L., Storch, H. H., and Fieldner, A. C. Conversion of Methane to Carbon Monoxide and Hydrogen. Ind. Eng. Chem., vol. 24, 1932, pp. 23–27; Chem. Abs., vol. 26, 1932, p. 1717.

Small-scale process has been developed for the conversion of CH_4 and steam or CO_2 into CO and H_2. The process is intermittent, 1st blasting the catalyst with a gas-air mixture followed by injecting the reaction mixture into the catalyst bed. Catalysts of Ni deposited on refractory proved most satisfactory for activity and durability. Optimum temperatures for reaction are 900°–1,000°, in which range nearly theoretical conversions were obtained.

Hayashi, S. *See* abs. 1344, 1345, 1346, 1349, 1350.

Hayes, A. *See* abs. 368, 854, 2214.

1371. Haynes, W. Wood Chemicals Meet Synthetic Competition. Jour. Chem. Education, vol. 24, 1947, pp. 109–113.

Abstract of a chapter in volume IV of the author's forthcoming book, A History of the American Chemical Industry, treating of the historical development of the synthetic MeOH process beginning with the work of Patart and the Badische Co. and following through the operations of the E. I. duPont de Nemours, Commercial Solvents, and other companies down to the present day.

Hays, G. E. *See* abs. 2220.

1372. Healey, F. H., Chessick, J. J., and Zettlemoyer, A. C. Adsorption of Gases on Metals. Am. Chem. Soc., 119th Meeting Abs., April 1951, p. 15 G.

Reduced and unreduced samples of Mo powder were studied by means of B. E. T. adsorption techniques. N, A, and O isotherms were measured at —195° and —183°. The Mo sample, originally 99.9% pure, was reduced with H_2 at several temperatures. The chemisorption of O_2 at —195° was taken to be a measure of the extent of reduced surface. Samples reduced at temperatures below approximately 500° showed no ability to chemisorb O_2, although there was an apparent increase in surface area. At about 540° some sintering was noted. Isosteric heats of adsorption were calculated for some of the reduced and unreduced surfaces. The value of V_m for the unreduced surface was found to be the same for A, N, and O. This finding led to a disagreement in areas calculated on the basis of closest packing of the adsorbate.

1373. Heat Engineering. Hydrogen Manufacture. Vol. 21, 1946, pp. 30–32.

Catalytic process is described that produces H_2 or a mixture of H_2 and CO in any ratio desired, from light hydrocarbons, such as natural gas, refinery gas, propane, or butane. Applicability of the process to synthesis of alcohols and to Fischer-Tropsch process is suggested. The H_2 produced varies in purity 98.5–99.9%. Gives simplified flow diagram.

1374. Hebden, D. Catalytic Synthesis of Methane From Carbon Monoxide and Hydrogen as a Means of Gas Enrichment. Thesis, Univ. of Leeds, 1943.

———. *See* abs. 690.

1375. Heckel, —. [Influence on the Grain Solidity of Cobalt Catalysts.] FIAT Reel K–29, 1938, frames 6,989–6,990, PB 70,218; TOM Reel 296.

Influences of various starting substances and additions and of various methods of precipitation, washing, forming, and reduction upon the grain solidification of the finished Co catalysts are tabulated.

1376. ———. [Examination of Kieselguhr.] FIAT Reel K–29, 1938, frame 7,029, PB 70,218; TOM Reel 296.

Compilation of the results of comparative washing tests on different test portions of kieselguhr, with 2 different cleansing apparatus, is given in a table. Differences in the results are explained by the different types of nozzles used.

1377. ———. [Thorium Content of Mixed Catalysts.] FIAT Reel K–29, 1938, frames 7,037–7,039, PB 70,218; TOM Reel 296.

Reduction of the Th content in mixed Th–Mg catalysts to about 2–3% ThO_2 is without noteworthy influence on the yield. 1 graph.

1378. ———. [Influence of the Reduction and the Type of Kieselguhr on the Catalytic Efficiency of Catalysts.] FIAT Reel K–29, 1938, frames 7,040–7,047, PB 70,218; TOM Reel 296.

It is established by tests that the method of reduction of catalysts with kieselguhr as carrier substance is without much influence, whereas, of all the kieselguhrs examined, the kieselguhr designated S–11 had the best reaction with regard to longevity and yield. 5 diagrams.

1379. ———. [Japanese Kieselguhrs as Carrier Substances for Catalysts.] FIAT Reel K–29, 1938, frames 7,048–7,056, PB 70,218; TOM Reel 296.

Japanese kieselguhrs are especially good as carrier substances for catalysts. 3 tables and 3 graphs.

1380. ———. [Tests on a New Catalyst Carrier—Eirichkorn.] FIAT Reel K–29, 1938, frames 7,077–7,081, PB 70,218; TOM Reel 296.

Results of a catalytic examination of catalysts, prepared by use of a new carrier called Eirichkorn are given but not described in detail. Compared to normal catalysts, Eirichkorn improved the activity of mixed Th–Mg catalysts, but deteriorated Th catalysts. 2 diagrams.

1381. ———. [Preparation of Cobalt Catalysts by Compression.] FIAT Reel K–29, 1938, frames 7,185–7,188, PB 70,218; TOM Reel 296.

It is shown that an increase of the Co density can be obtained by repeated pressing under dust conduction. The influence on the activity of such compressed catalysts is still being examined. 2 graphs.

1382. ———. [Use of Nickel and Cobalt-Nickel Catalysts in the Gasoline Synthesis.] FIAT Reel K–29, 1938, frames 7.316–7.319, PB 70,218; TOM Reel 296.

It is possible to prepare, by use of appropriate activators, a mixed Co–Ni catalyst with more than 50% Ni, which, in the normal pressure synthesis, does not produce a smaller yield compared to the pure Co catalyst. A Ni catalyst of equal value cannot be made as yet. The reaction of the Co–Ni mixture in the medium pressure process has still to be worked out. 1 table.

1383. Heckel, H. [Influence of Kieselguhr on the Activity of the Catalyst.] FIAT Reel K–20, frames 103–108, 1937, PB 70,211; TOM Reel 287.

Tests were made covering chemical components. physical properties, microscopic structure, and activity. The solubility in acid and H_2O has no influence on the activity. Physical tests showed that a high loss of ignition diminishes the activity of the catalyst.

———. *See* abs. 402, 2875, 2876.

Hedin, R. *See* abs. 1385, 1387.

Hedley, T. J. *See* abs. 2319.

Hedvall, J. A., and Berg, A. [Magnetic Transformation and Catalytic Activity. VI. Catalytic Experiments with $MgO.Fe_2O_3$ and Different Kinds of Iron and Steel in the Region of the Loss of Their Ferromagnetic Properties.] *See* abs. 1389.

Hedvall, J. A. and Byström, H. [Magnetic Transformation and Catalytic Activity. V. Course of the Catalytic Hydrogenation of Liquid Unsaturated Compounds in the Region of the Curie Interval of Ferromagnetic Catalysts.] *See* abs. 1388.

1384. Hedvall, J. A., and Gustavson, E. [Catalytic Activity and Ferromagnetism. I.] Svensk Kem. Tid., vol. 46, 1934, pp. 64–65; Chem. Abs., vol. 28, 1934, p. 4971.

It has been shown recently that the reactivity of solids is increased by phase transformations that do not affect the lattice structure. Hence, it is important to investigate whether the disappearance of ferromagnetism produces a similar change. For this purpose experiments were made on the reaction $N_2O=N_2+O$, with pure Ni as the catalyst, at 330°–380°, since no alteration in the Ni lattice has been observed in a temperature interval of 1,000°. Between 330° and 359° the decomposition was constant, but at approximately 359° there was an abrupt rise in the decomposition-temperature curve. The Curie temperature for this specimen of Ni was 358°–360°. Control experiments with N_2 or O_2 instead of N_2O gave curves without this sharp break, as did experiments with N_2O over NiO. Experiments with other samples of Ni with different Curie points showed the same agreement between the temperature at which the break occurs and the Curie temperature. The sudden application of a magnetic field, either above or below the Curie point, produced no appreciable effect on the decomposition.

1385. Hedvall, J. A., Hedin, R., and Persson, O. [Ferromagnetic Transformation and Catalytic Activity. II] Ztschr. physik. Chem., vol. 27, B, 1934, pp. 196–208; Chem. Abs., vol. 29, 1935, p. 1314.

Catalytic effect of Ni on the reaction $N_2O \rightarrow N_2+O$ is suddenly changed at the Curie point, where the amount decomposed increases rapidly. This is another example of the theory of the change of reactivity in transitions that do not result in the change of the lattice symmetry.

1386. Hedvall, J. A., and Sanford, F. [Effect of Ferromagnetic Transformation on the Catalytic Power of Nickel in the Reaction $2\,CO=CO_2+C$. III.] Ztschr. physik. Chem., vol. 29, B, 1935, pp. 455–463; Chem. Abs., vol. 30, 1936, p. 369.

Four kinds of Ni catalysts were prepared and carefully analyzed for impurities. The Curie point was determined for each. The reaction $2\,CO=CO_2+C$, catalyzed with this Ni, was then studied, and, as with other reactions, the rate increased sharply at the Curie point. The effect of impurities on the reaction also was studied, as well as the condition of formation of Ni carbide and its effect on the reaction.

1387. Hedvall, J. A., and Hedin, R. [Ferromagnetic Conversion and Catalytic Activity. IV. Hydrogenation of Carbon Monoxide and Ethylene Over Nickel and Carbon Dioxide Formation From Carbon Monoxide Over the Heusler Alloy, $MnAlCu_2$.] Ztschr. physik. Chem., vol. 30, B, 1935, pp. 280–281; Chem. Abs., vol. 30, 1936, pp. 1621–1622.

Rates of the reactions change discontinuously at the Curie point when the ferromagnetic properties of the catalyst disappear. A commercial thermal-conductivity apparatus was used successfully for analysis of the $CO–CO_2$ mixture.

1388. Hedvall, J. A., and Byström, H. [Magnetic Transformation and Catalytic Activity. V. Course of the Catalytic Hydrogenation of Liquid Unsaturated Compounds in the Region of the Curie Interval of Ferromagnetic Catalysts.] Ztschr. physik. Chem., vol. 41, B, 1938, pp. 163–166; Chem. Abs., vol. 33, 1939, p. 458.

Hydrogenation of castor oil and cottonseed oil was studied in the presence of the catalysts Ni–Cu and Pd–Co and in the region of the Curie point (150°–200°). A sudden increase in the catalytic activity is noted at the Curie point.

1389. Hedvall, J. A., and Berg, A. [Magnetic Transformation and Catalytic Activity. VI. Catalytic Experiments With $MgO\cdot Fe_2O_3$ and Different Kinds of Iron and Steel in the Region of the Loss of Their Ferromagnetic Properties.] Ztschr. physik. Chem., vol. 41, B, 1938, pp. 388–395; Chem. Abs., vol. 33, 1939, p. 1579.

Reactions of $2\,CO+O_2=2\,CO_2$, $CO+H_2=C+H_2O$ and $CO+3\,H_2=CH_4+H_2O$ were studied on the catalysts synthetic Mg ferrite, pig Fe, and a W–Cr steel. The activity of the catalysts increases at the Curie point.

Hedvall, J. A., and Hedin, R. [Ferromagnetic Conversion and Catalytic Activity. IV. Hydrogenation of Carbon Monoxide and Ethylene Over Nickel and Carbon Dioxide Formation From Carbon Monoxide Over the Heusler Alloy, $MnAlCu_2$.] *See* abs. 1387.

Hedvall, J. A., and Sandford, F. [Effect of Ferromagnetic Transformation on the Catalytic Power of Nickel in the Reaction $2\,CO=CO_2+C$. III.] *See* abs. 1386.

Hedvall, J. A., Hedin, R., and Peterson, O. [Ferromagnetic Transformation and Catalytic Activity. II.] *See* abs. 1385.

1390. Heidenreich, R. D., Sturkey, L., and Woods, H. L. Decomposition of Martensitic Steel Above and Below 300°. Nature, vol. 157, 1946, p. 518; Chem. Abs., vol. 40, 1946, p. 5382.

Electron microscope and electron-diffraction methods were used to study metallurgical structures in a plain C steel, 0.9%, 0.15% Si, 0.0056% N. Martensite aged at 200° gives a fine dispersion of hexagonal Fe_3N but no Fe_3C. Above 300° the reaction product is Fe_3C. A specimen aged at 200° shows both Fe_3N and Fe_3C after 30 min. at 350°. A mechanism is suggested: (1) $Fe+C_{solution}$, $+N_{solution}$, martensite, $\xrightarrow{200°} Fe_3N$ or $Fe_3(CN)+C_{solution}$; (2) $Fe+C_{solution}$, martensite, $\xrightarrow{400°} Fe_3C+N_{solution}$; (3) Fe_3N or $Fe_3CN+C_{solution} \xrightarrow{350°} Fe_3C+N_{solution}$. The preparation of satisfactory surfaces involved (1) abrasion through 4/0 metallographic paper; (2) electrolytic polishing; (3) etching 60–90 sec. in 2% HCl and 1% $FeCl_3$ in MeOH; (4) rinsing (a) 50:50 Me_2CO–MeOH+0.5% HCOOH, (b) 50:50 Me_2CO–MeOH, (c) dry C_6H_6; (5) drying in an air blast.

Hein, L. B. *See* abs. 701a.

1391. Heinemann, F. Fischer-Tropsch Hydrocarbon Synthesis—Its First Development. Petrol. Refiner, vol. 28, No. 1, 1949, pp. 126–127.

Brief account of the patent development of the Fischer-Tropsch process, with biographical notes and photographs of the inventors.

1392. Heinemann, H. Digest of United States Patents on the Recovery and Processing of Natural Gas and Its Constituents and on Hydrocarbon Synthesis. Petrol. Refiner, vol. 23, No. 7, 1944, pp. 172, 174, 178, 180, 182, 184.

15 United States patents dealing with synthesis of hydrocarbons from CO and H_2.

1393. ———. Foreign Processes for the Conversion of Methane to Hydrogen and Carbon Monoxide. Petrol. Refiner, vol. 23, No. 1, 1944, pp. 35–36; Chem. Abs., vol. 39, 1945, p. 2391.

Review with 16 refs.

1394. ———. Digest of United States Patents on Hydrogenation of Hydrocarbons and Carbon Monoxide. Petrol. Refiner, vol. 25, No. 1, 1946, pp. 168, 170, 172.

Abstracts of 27 United States patents from 1944 and 1945.

1395. Heisenberg, W. [Theory of Ferromagnetism.] Ztschr. Physik, vol. 49, 1928, pp. 619–636; Chem. Abs., vol. 22, 1928, p. 4348.

An attempt to explain the Weiss molecular field on the basis of a quantum mechanics energy-interchange process similar to that recently applied by Heitler and London to the interpretation of homopolar valence forces. According to this, ferromagnetism is possible only when (1) the lattice is such that each atom has at least 8 neighbors, and (2) the principal quantum number of the electrons responsible for the magnetism must be ≤ 23. These conditions together do not serve to distinguish Fe, Ni, and Co from all the other materials but Fe, Ni, and Co satisfy these conditions. The present paper is, therefore, regarded by Heisenberg as preliminary and further development is promised.

1396. Held, W. [Production of Gases for Syntheses.] Petrol. Ztschr., vol. 35, No. 25, 1939, pp. 435–437; Chem. Abs., vol. 33, 1939, p. 9559.

Various processes for the production of gases to be used in syntheses are described; for example, H_2 or mixtures of H_2 with N_2 or CO, according to the Winkler, Koppers, Pintsch-Hillebrand, Wintershall-Schmalfeldt, Bubiag-Didier, and Lurgi methods.

1397. ———. [Production of Hydrocarbons by Synthesis.] Petrol. Ztschr., vol. 35, 1939, pp. 493–495; Chem. Abs., vol. 34, 1940, p. 240.

Surveys coal-hydrogenation process and the Fischer-Tropsch synthesis very briefly. Gives some figures on the requirements of Fischer-Tropsch plants, including data on quantities of H_2 needed and amounts of metals required for furnaces and containers. The influence of catalyst, temperature, and pressure is discussed.

Hellbrügge, J. *See* abs. 163.

1398. Heller, O. [Production of Water Gas and Gas for Synthesis From Pulverized Fuels.] Chim. et ind., Special No., June 1933, pp. 466–467; Chem. Abs., vol. 27, 1933, p. 5937.

So-called cellular gas producer, German Patent 520,739, is described. In it a high-grade water gas can be produced by treating pulverized coal with steam superheated to 1,000°. With a specially designed producer and air heated to a high temperature, gas of suitable composition for the synthesis of NH_3 can be produced directly from bituminous coal. By combining the process with a treatment with O_2, water gas virtually free from CH_4 and N_2 and suitable for the production of H_2 can be produced. The possibility of easily regulating the temperature and the amount of steam permits obtaining a mixture of CO and H_2 for the synthesis of MeOH. Gasification and cracking of tar and mineral oils can be carried out efficiently. Tars and mineral oils can readily be treated to obtain either a high calorific gas or mixtures of hydrocarbons with high gasoline and benzene contents.

Heller, W. *See* abs. 3064.

1399. Helmers, C. J., Clark, A., and Alden, R. C. Catalytic Treatment of Synthetic Gasoline. Oil Gas Jour., vol. 47, No. 26, 1948, pp. 86, 89, 91, 92.

In the synthesis of olefinic gasoline from CO and H_2 with a fluidized Fe-base catalyst, the oxygenated compounds remaining therein must be removed as they have properties undesirable in a motor fuel. Since they are present only in small amounts, their removal does not materially affect the octane rating of the fuel. Any major improvement in octane rating of the synthetic gasoline, therefore, requires improvement in the rating of the hydrocarbons present. In the case of olefins, this is most readily accomplished by isomerization. The Perco catalytic desulfurization process was investigated in connection with this upgrading of olefinic synthetic gasolines. Briefly this process entails a mild vapor-phase treatment of the gasoline over bauxite catalyst. The gasoline is vaporized and preheated to 700°–800° F., and the superheated vapors are passed through the catalyst bed at 30–50 lb. pressure. The flow rate is 1–3 vol. of gasoline per hour per vol. of catalyst, or approximately 150–450 bbl. of gasoline per ton of catalyst per day. The results show a considerable improvement in the octane number up to a maximum in the temperature range 700°–750° F. at a constant flow rate of 1.5 vol. gasoline per vol. of catalyst per hr. Doubling the flow rate and increasing the temperature to 850° F. gives about the same octane improvement. It is assumed that the isomerization is primarily a shift of the double bond rather than a branching of the chain. Improvement was noted in the blending value of Perco treated gasoline with polymer gasoline, the gum content, and the storage stability. The oxygenated compounds originally present in the synthetic gasoline appear to be decomposed in passing through the catalyst bed, as is evident from the composition of the gas produced in the treatment.

1400. Hendricks, S. B. Crystal Structure of Cementite. Ztschr. Krist. (in English), vol. 74, 1930, pp. 534–545; Chem. Abs., vol. 24, 1930, p. 5560.

From data published by Westgren and Phragmen a complete structure determination is made for Fe_3C. The space group is *V16/h*. Atomic positions are derived. The structure is of the coordination type.

———. *See* abs. 390, 836.

1401. Henk, H. J. [Inhibiting the Autoxidation of Fats and Oils.] Seifensieder-Ztg., vol. 64, 1937, p. 942; Chem. Abs., vol. 32, 1938, p. 1961.