to the sum of the thermal values of the raw materials used and of the heat and power consumed. It is apparent that complete conversion of coal to gas in a water-gas plant, which has had some application in the United States, must be thermally more efficient than the separate production of coal gas and water gas. It may be calculated that the advantage is about 12%. The Fuel Research Station, by adopting a special cycle, has gasified bituminous and sub-bituminous coals in a water-gas generator at a thermal efficiency of 64%. Data are given for several processes. The Tully, Humphreys-Glasgow (thermal efficiency 57% including the fuel for steam raising), Travers-Clark, and Broadhead (62% excluding power and steam) processes exemplify the type of combination carbonization and water-gas plant. The German processes for complete gasification have received more intensive development for 3 reasons: To utilize brown coal, to produce CO: H₂ mixtures for synthesis gas, and to make use of industrial O₂. They fall into 3 classes: (a) Those that involve heating by the recirculation of hot gases, for example, Pintsch-Hillebrand, Koppers, and Wintershall-Schmalfeld, which gasify brown coal at an over-all thermal efficiency of 50%; (b) those that involve an externally heated reaction chamber, for example, Heller, Ahrens (78.2% efficiency), Strache, and Didier-Bubiag (68.7% efficiency), have had industrial success as a flexible means of making synthesis gas at a CO: H₂ ratio of 2) ; (c) those that involve the use of O₂, for example, Winkler (77% excluding O₂ production), Lurgi-Drawe (62.2%, this process has probably reached the peak of efficiency under present operating conditions), Thyssen-Galoczy (80% including O₂ production). The special advance of this last group has been brought about by the use of O₂ made available from synthetic NH₃ plants. If O₂ were made specially for the purpose, the cost would be much higher. The development of a fairly cheap O₂ plant for application in the gas industry is one of the pressing problems.

1767. ———. Synthesis of Methane. Gas World, vol. 122, 1945, pp. 196–200, 209; Gas Times, vol. 42, Supp., 1945, pp. 1–4; Chem. Abs., vol. 39, 1945, p. 2189.

Review of research and a discussion of the reactions involved in synthesizing CH₄ from water gas and the application of these reactions to the production of city gas. With a high H₂: CO ratio and when the main reaction at a low temperature and atmospheric pressure is

$$CO+3H_2 \rightleftharpoons CH_4+H_2O, \quad (1),$$
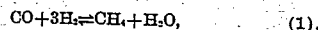
the water-gas-shift reaction must be satisfied:

$$CO+H_2O \rightleftharpoons CO_2+H_2. \quad (4)$$
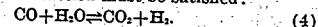
If the H₂: CO ratio is reduced, reaction (4) becomes more effective and more CO₂ appears in the final gas. When the ratio reaches unity, the reaction is:

$$2CO+2H_2 \rightleftharpoons CH_4+CO_2. \quad (2)$$
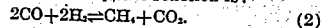
The effect of increase of temperature is to favor the water-gas reaction (4) at a high ratio and the CH₄ reaction (1) at a low ratio. A constant CO₂: CH₄ ratio independent of the H₂: CO ratio is suggested at a temperature of about 750° C. The effect of pressure up to 25 atm. is nil at 300° but reduces the effect of increasing temperature. At 300° and 1 atm., the percentage of CH₄ obtainable in the dry CO₂-free gas rises from 83 to 98% as the H₂: CO ratio falls from 3:1. With increase of temperature the % of CH₄ falls until it is less than 10% at 700°; a gas containing 50% CH₄ is obtained at 500° when the pressure is 1 atm. and at 700° when the pressure is 25 atm. In operating a technical process, assuming the use of a catalyst active enough to bring reactions (1) and (4) to completion at a high space velocity, the most favorable conditions for obtaining a gas of high CH₄ content would be low temperature and atmospheric pressure what-

ever the H₂: CO ratio. At a higher temperature, however, the CH₄ content would be maintained and catalyst activity preserved only by increasing the working pressure. Care must be taken to prevent deterioration of the catalyst by surface overheating and bringing on reaction:

$$2CO \rightleftharpoons CO_2+C. \quad (5)$$

The deposition of C can be suppressed by using a high H₂: CO ratio, which favors reaction (1). To obtain a ratio of 3:1, it may be necessary to treat part of the water gas with steam

$$H_2+CO+H_2O \rightleftharpoons CO_2+2H_2 \quad (6)$$
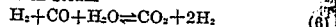
and to remove the CO₂ by washing under pressure, thus increasing the H₂ content of the original gas to the desired figure. Ni catalysts have been developed that can be operated at a high space velocity and that have an initial activity many times greater than is necessary to carry the main reactions to equilibrium. The reactions have been subjected to close study, and the knowledge collected is being applied to the control of the reaction on a larger scale looking towards the development of a pilot plant to operate under the proved conditions.

1768. ———. Control of Chemical Reactions on a Large Scale. Gas Times, vol. 51, 1947, pp. 369–372; Inst. Gas. Eng., Commun. and Repts., Commun. 315; Gas World, vol. 126, 1947, pp. 779–786, 808; vol. 127, pp. 93–98; Chem. Abs., vol. 41, 1947, p. 7015.

A presentation of the principles of the fluidized technique and a review of its development in the fields of petroleum refining, hydrocarbon synthesis, and coal gasification. Several advantages are evident: (1) The constant uniformity of temperature control obtainable; (2) the elimination of undesirable hot-spots in catalyzed reactions by the rapid mixing and turbulence of particles; (3) the achievement at high efficiency of high rates of heat transfer; (4) the high reaction rates obtainable because of the large surface available, the scrubbing action of gases in reducing protective layers, and the maintenance of deep reaction beds under uniform conditions; and (5) the convenient and cheap method of movement of large quantities of solids.

———. See abs. 451, 452, 453, 1466, 1467, 3198.

1769. KINGMAN, F. E. T. Adsorption of Hydrogen by a Zinc Oxide–Chromium Oxide Catalyst. Trans. Faraday Soc., vol. 27, 1931, pp. 654–661; Chem. Abs., vol. 26, 1932, p. 355.

Adsorption of H₂ on a ZnO–Cr₂O₃ catalyst was studied at —80°, 0° and 100°. 3 types of adsorption probably occur, 1 at low temperature, involving a low energy of activation, another at higher temperatures involving a high energy of activation but not leading to the reduction of the catalyst, and a 3d at high temperature, leading to reduction of the catalyst.

———. See abs. 450, 1144, 1145.

1770. KINGMAN, F. E. T., AND CAWLEY, C. M. Cracking of Middle Oil From the Fischer-Tropsch Process. Petroleum (London), vol. 9, 1946, pp. 126–128; Chem. Abs., vol. 40, 1946, p. 5903.

Experiments were carried out on the thermal cracking of the middle oil fraction, boiling at 200°–300°, from Fischer-Tropsch product, using a vertical, electrically heated, Pyrex tube with a 35-ml. reaction space. The cracking temperature varied from 570°–635°, the throughput from 40–110 gm. per hr., and the reaction time from 30–10 sec. At 635° and a throughput of 90 gm. per hr., the total yield of liquid product was 67.6 wt. % of the original oil, with a yield of gasoline to 200° of 20.4%. Recycling the oil boiling above 200° gave a total yield of 37.8% of gasoline to 200°; Br No. 130, and a yield of gas of 39.3 l. per 100 gm. of raw material. The gasoline to 170° had a Br number of 148, and contained approximately 80–90% olefins

with less than 2% aromatics. The gaseous product from thermal cracking contained only a small proportion of H₂; the olefins, which increased from 57% at 570° to 63% at 635°, consisted mainly of C₂H₄ and C₃H₆ with a smaller proportion of C₄H₈ and a very small amount of butadiene. With a catalyst of mixed alumina and silica, the yield of gas increased and the nature of the products was noticeably affected. The gasoline had a lower olefin content and a higher content of both aromatic and saturated hydrocarbons. The gas contained a greater proportion of H₂; the proportion of total olefins was not greatly changed, but the catalyst favored the production of C₂H₄ and C₃H₆ in place of C₂H₆, and the formation of butadiene was completely suppressed.

1771. KINGTON, G. L., BEEBE, R. A., POLLEY, M. H., AND SMITH, W. R. Entropy of Adsorbed Molecules. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1775–1781; Chem. Abs., vol. 44, 1950, p. 6228.

Differential heats of adsorption of N₂ and O₂ on TiO₂ were determined calorimetrically at 78.5° K. The TiO₂ used in both cases was a sample of anatase with a Brunauer, Emmett, and Teller (abs. 389) surface area of 13.9 m.² per gm. The magnitude of the heat in both cases indicates that the adsorption is van der Waals in nature. The initial increments of N₂ showed a heat of adsorption approximately 1 kcal. per mol. higher than the initial O₂ values. The partial molal entropy of the adsorbed gas was determined from experimental data for both N₂ and O₂ adsorbed on C black and TiO₂ (anatase) at 78.5° K. The results show that the partial molal entropy of the adsorbed gas is less than the partial molal entropy of the bulk 3-dimensional liquid or solid phases, at coverages less than a monolayer, as defined by B. E. T. v_m, for all the systems investigated. At coverages greater than a monolayer, the partial molal entropy approaches the entropy of the 3-dimensional liquid or solid. The entropy requirements of the B. E. T. theory are shown to be incompatible with experimental evidence at coverages less than a monolayer.

KINI, K. A. See abs. 1192, 1193, 1193a.

1771a. KINI, K. A., BASAK, N. G., AND LAHIRI, A. Adsorption of Hydrogen and of Carbon Monoxide on an Iron–Copper–Magnesia Catalyst. Jour. Sci. Ind. Research (India), vol. 10B, No. 10, 1951, pp. 243–245; Chim. et ind., vol. 67, 1952, p. 790.

Adsorption of H₂ and CO on a Fischer-Tropsch catalyst (Fe–Cu–MgO, 80:5:15) was determined between 99° and 249°. The results show that synthesis of hydrocarbons is realized by chemical adsorption. In order for the synthesis to occur under the best conditions, it is essential that chemical adsorption of CO should exceed that of H₂.

1772. KINNEY, C. R. Nonfuel Uses of Bituminous Coal. Proc. Coal Min. Inst. America, 58th Ann. Rept., Dec. 7, 1944, pp. 1–11.

Brief mention of the use of coal for making water gas from which MeOH and synthetic gasoline can be made by the Fischer-Tropsch process.

KIPERMAN, S. See abs. 3367, 3369.

1773. KIPERMAN, S., AND TEMKIN, M. [Kinetics of Ammonia Synthesis on Molybdenum Catalyst.] Acta Physicochem. U. R. S. S. vol. 11, 1946, pp. 267–282; Jour. Phys. Chem. (U. S. S. R.), vol. 20, 1946, pp. 369–378; Chem. Abs., vol. 40, 1946, p. 6950.

Experimental data confirm the work of Temkin and Pyzhev on the synthesis of NH₃ on promoted Fe catalyst and extend the results to a Mo catalyst. A flow system was used with 2 cc. of catalyst. The Mo-catalyst was prepared by reducing ammonium molybdate in NH₃ for 20 hr. at 600°–650°. X-ray diffraction patterns indicate that the catalysts operate in the form of metallic

Fe and Mo₂N. The data for both catalysts support the kinetic equation suggested by Temkin and Pyzhev, the value of α for both catalysts is 0.5. The apparent activation energy of NH₃ decomposition on Mo catalyst as calculated from the synthesis rate is 42.5 kcal. per mol. The NH₃ synthesis on Fe and Mo is considered to have the same mechanism.

1774. KIPNIS, F. Separation of Catalysts from Hydrogenation Reaction Mixtures. Ind. Eng. Chem., anal. ed., vol. 16, 1944, p. 637; Chem. Abs., vol. 39, 1945, p. 3.

A filter aid, such as Dicalite 4200, is used with a Büchner funnel to give a clear filtrate.

1775. KIRKBY, W. A. Oil From Coal in Japan. Fuel, vol. 23, 1944, pp. 32–33.

Notes on recent developments in fuel technology.

1775a. KIRKPATRICK, W. J. Nickel Sulfide Catalysts. Advances in Catalysis, Academic Press, Inc., New York, vol. 3, 1951, pp. 329–339.

A number of reactions catalyzed by Ni sulfide are given and the conditions under which Ni sulfide acts as catalyst are mentioned. The 2 Ni sulfides, Ni₃S₂ and NiS, which can exist under conditions prevailing in some catalytic systems, are catalysts for some reactions also catalyzed by metallic Ni and for other reactions not yet found to be catalyzed by the metal. Explanations of this behavior in terms of bond theory or Brillouin zones can be expected in the near future. 19 refs. are given.

1776. KIRSCHFELD, L. [Water-Gas Equilibrium in Homogeneous and Heterogeneous Reactions.] Chem. Tech., vol. 18, 1945, pp. 52–59.

Graphic methods are used for determining the water-gas equilibrium (1) for constant C content, (2) for constant O₂ content, and (3) for interaction of the gas with Fe and Fe oxides.

KIRSCHT, P. H. See abs. 3057, 3059.

KISTIAKOWSKY, G. B. See abs. 1419, 3336.

1777. KITA, G. Catalyst for Production of Synthetic Gasoline. Jour. Fuel Soc. Japan, vol. 16, 1937, pp. 497–511, in English, pp. 60–62; Jour. Inst. Petrol. Technol., vol. 23, 1937, p. 362A; British Chem. Abs., 1937, B, p. 1005; Chem. Abs., vol. 31, 1937, p. 6858.

Further discussion is presented on the suitabilities of different types of catalysts used in the production of synthetic gasoline in the Fischer process. Co catalysts with accelerators, particularly ThO₂ and U₂O₆, give good yields, the quantity required being reduced to ⅙ if pumice is used as the carrier. Increased yields are given by the addition of sucrose which increases the porosity by decomposition of Co(NO₃)₂ at high temperatures. Ni catalysts are highly susceptible to manufacturing conditions and should be prepared by settling with the addition of alkali carbonate, and reduction should be carried out at 450° C., while the Ni should not contain more than 0.5%, and must contain an irreducible oxide accelerator plus a small quantity of alkali. The substitution of Al₂O₃ or acid clay for ThO₂ as an accelerator gave improved results. Alloy catalysts made from Ni–Co–Al–Si alloy from which Al or Si is extracted with alkali have the advantage of small volume, high thermal conductivity, and granular form. Ni–Co catalysts of composition 50% Co–50% Ni+15% Mn+3% ThO₂+5% U₂O₆+125% diatomaceous earth gave the highest yield of gasoline obtained in these tests, 166 cc./m.³ of gas. Fe catalysts are of low activity, producing about ⅛ of the yield of gasoline given by more effective catalysts.

1778. ———. Artificial Petroleum. Chem. Rev. (Japan), vol. 4, 1938, pp. 436–449; Chem. Abs., vol. 35, 1941, p. 7679.

Lecture.

1779. ——. Synthetic Petroleum From Water Gas by Iron Catalyst. Chem. Rev. (Japan), vol. 7, 1941, pp. 203–208; Chem. Abs., vol. 35, 1941, p. 7679.

A lecture with figs.

KLAPCHUK, S. V. See abs. 1267.

1780. KLAR, M. [Technical Preparation of Formaldehyde.] Chem.-Ztg., vol. 59, 1935, pp. 741–744; Chem. Abs., vol. 29, 1935, p. 7277.

World production of HCHO, 40 vol. %, amounts to about 75,000 tons/yr., almost wholly from MeOH. 85% of which is produced synthetically from water gas.

KLAS, H. See abs. 3056.

1781. KLEINSCHMIDT, R. V. Handling High Pressures in Chemical Synthesis. Chem. and Met. Eng., vol. 40, 1933, pp. 361–364; British Chem. Abs., 1933, B, p. 815.

Soft Fe and Cu are suitable gasket materials for high-pressure joints, but Cu cannot be used where temperature variations are encountered. The use of soft Fe in grooves is indicated. Joints in which rubber packing is pressed outward by the fluid pressure against the gasket are satisfactory, but not at higher temperature. The use of 2 valves in series enables the second valve to be closed under favorable circumstances. Flow control valves are often fitted with a coil of small high-resistance tubing to dissipate the energy of expansion. The use of valves utilizing the principle of the labyrinth packing gland is suggested. Compressors should be designed for the particular gas with which they have to deal. In the design of converters provision should be made for (1) an outer curtain of incoming gas to act as an insulating medium, (2) a countercurrent heat exchanger with preferably small tubes of considerable length, (3) generally concurrent heat transfer from the catalyst bed to render the bed thermally stable and to prevent too great a range of temperature in the bed.

——. See abs. 1080.

1782. KLEMENC, A., AND RUPP, J. [Behavior of Iron Catalysts in the Temperature Range of 250°–450° Toward Illuminating Gas and Other Similar Gases.] Angew. Chem., vol. 47, 1934, pp. 182–184; Chem. Abs., vol. 28, 1934, p. 3221.

Behavior of commercial illuminating gas was investigated in the presence of the following Fe catalysts: (1) Fe precipitated from $Fe(CO)_5$, (2) Fe powder, (3) Fe powder activated by treatment with $AlCl_3$ and NH_4 OH or NaOH solutions and (4) synthetic catalysts, for example, Fe oxides from various sources. A reduction of the CO content and an increase of the CH_4 content take place. The most effective temperature range for the experimental conditions was found at 280°–450°. A greater retort length results in greater CO conversion, while increasing gas velocity results in smaller CO conversion. The catalyst surface undergoes a continual change, and the progress of the reaction dilutes the catalyst. As side reactions the decomposition of heavier hydrocarbons and reactions with H_2O vapor were encountered, but it was found that temperatures can be chosen low enough to avoid the decomposition of the heavier components; however, larger quantities of H_2O vapor act disturbingly upon CH_4 formation. Attempts to regenerate the catalysts by simple processes failed, and it was found that a mixture of 21–22% C and 32–34% Fe, with a ratio of Fe : O_2=3 : 4.1, becomes inactive. At a gas velocity of 500 l. per hr. (area=81.6 cm.^{3}), a consumption of 10 gm. catalyst per m.^{3} of converted gas was determined, after a passage of 140 m.^{3} of gas, and the catalyst was still in a decidedly active condition.

1783. KLEMM, H. [Type of Structure in the Iron-Carbon System.] Arch. Metallkunde, vol. 3, 1949, pp. 265–271; Chem. Abs., vol. 44, 1950, p. 507.

Fe–C diagram is analyzed and photomicrographs show the various transition and equilibrium phases as they accur. Typical structures resulting from the method of production and as a result of segregation are shown.

1784. KLEMM, R. [Fused-Iron Catalysts for Carbon Monoxide–Hydrogen Synthesis.] TOM Reel 278, item 2, 44 pp.; PB 82,353; FIAT Rept. 1267, Supp., 1949, 39 pp.; PB 97,368 S.

Summary of observations and experience gained during 8 years of experimentation with the development of fused Fe catalysts used in CO–H_2 synthesis under high pressure and temperature. The catalysts discussed were produced by fusing Fe and the additives in a stream of O_2. Microscopic examination is described in detail. The effect of basic and acidic additives and of lattice displacement and disturbance on the effectiveness and yield of the catalysts is studied. The most advantageous location of the additive in the lattice is given. The results obtained with various catalysts of this type are presented.

1785. KLEMPT, W. [Contact Furnaces and Contact Equipment in the Chemical Industry.] Ztschr. Ver. deut. Ing., Beih. Verfahrenstech., vol. 83, 1939, pp. 122–127; Chem. Abs., vol. 34, 1940, p. 4.

Discussion of most-important types of equipment for catalytic gas reactions with figures and 12 refs.

——. See abs. 1724.

1786. KLEMPT, W., AND BRODKORB, F. [Methane-Steam Equilibrium and Its Control.] Ber. Gesell. Kohlentech., vol. 3, 1930, pp. 220–229; British Chem. Abs., 1931, B, p. 325.

Theoretically, at high temperatures the reaction between CH_4 and steam takes place according to the equation (1) $CH_4 + H_2O = CO + 3H_2 - 48.9$ kcal., while at lower temperatures it takes the form (2) $CH_4 + 2H_2O = CO_2 + 4H_2 - 38.5$ kcal. The equilibrium constants for these two reactions have been determined only for a few temperatures, but it is possible to calculate their values from those obtained in the reactions $CH_4 = C + 2H_2$; $C + CO_2 = 2CO$; and $CO + H_2O = CO_2 + H_2$, which are known over the range 450°–1,200°. The constants $K'_p = p_{CH_4} \cdot p_{H_2O}/p_{CO} \cdot p_{H_2}$ and $K''_p = p_{CH_4} \cdot p_{H_2O}^2/p_{CO_2} \cdot p_{H_2}^4$ are tabulated over the same range, but it is emphasized that the values of K'_p can only be strictly accurate at very high temperatures, while the applicability of those of K''_p is limited to lower temperatures. Calculation of the equilibrium condition shows that at 500° the cracked gas contains CH_4, 33.3%; CO, 8.33%; and H_2, 25.0%; while at 940° the composition is CH_4, 0.505%; H_2O, 0.505%; CO, 24.8%; and H_2, 74.1%; when reaction (1) takes place. A similar table is given in connection with equation (2). Since in practice an excess of steam would be used, calculations have been made to find the effect of 2-fold and 6-fold excess of steam on the equilibrium when pure CH_4 is used. The influence is considered of the other constituents on the equilibrium amount of CH_4 present in a gas of the following composition: 10% $(CO + CO_2)$, 30% $(CH_4 + C_nH_m)$ 50% H_2, 10% N_2. Temperature-composition graphs are given for both reactions (1) and (2) with this mixture. At about 820° the CH_4 decomposes to give at equilibrium a gas containing equal proportions of CO and CO_2.

1787. ——. [Water-Gas Equilibrium and Its Control.] Ber. Gesell. Kohlentech., vol. 3, 1930, pp. 261–274; British Chem. Abs., 1931, B, p. 325.

Theoretically, the known values for the equilibrium constant of the reaction $CO + H_2O = CO_2 + H_2$ over the range 327°–2,090° indicate that at higher temperatures the equilibrium is in favor of CO-steam. To favor the production of H_2, as low a temperature as is compatible with suitable reaction velocity must be chosen. The

use of catalysts alone does not materially assist in the complete removal of CO from the gas at temperatures at which it is practicable to work. The theory is discussed of the disturbance of the equilibrium by use of excess of steam and by removal of the CO_2 formed simultaneously with the H_2 by absorbents such as lime. The pressure of CO_2 in the system $CaCO_3$–CaO–CO_2 limits the temperature at which the latter method of disturbing the water-gas equilibrium can be used to an extreme of 600°. In practice, lower temperatures would have to be used. This theoretical study leaves no doubt that the removal of CO_2 is the more practicable method of achieving a good conversion of the CO. Thus, at 550°, to reduce the steam-and CO_2-free gas to the same CO content as that produced by the passage over lime, using 1 vol. of steam, requires a volume of steam 20 times that of the CO. By using a slight excess of steam in conjunction with CO_2 removed at this temperature, the CO can be reduced to a mere trace. The foregoing considerations are applied to the gas resulting (abs. 1724) from the action of steam and air on CH_4.

1788. KLEPPA, O. J. [Equilibrium $CoO + H_2 = Co + H_2O$. The Molar Entropy of Cobaltic Oxide.] Svensk Kem. Tid., vol. 55, 1943, pp. 18–25; Chem. Zentralb., 1943, I, p. 1970; Chem. Abs., vol. 38, 1944, p. 4855.

Equilibrium was studied by the stream method, and values were obtained that agree with the static method. For the constant $K_p = p_{H_2O}/p_{H_2}$ the heterogeneous equilibrium gives $K_p^{595} = 39.35$, $K_p^{849} = 44.2$, $K_p^{1012} = 51.3$, $K_p^{728} = 56.8$ (temperature in degrees Kelvin). According to $\Delta F = -RT \log K_p$, the change in free enthalpy (reaction-work) can be calculated, and also the heat content by means of van't Hoff's equation, which then can be determined at other temperatures with the help of molecular heat. The normal values $\Delta F^{298} = -3461$ cal. per mol., and $W_p^{298} = 859$ cal. per mol., are obtained, from which it follows that $\Delta S^{298} = 8.73$ cal. per mol. per degree. From the known normal entropies of H_2O, Co, and H_2 it follows that S^{298} Co = 11.94 ± 0.2 cal. per deg. mol.

1789. KLIMOV, B. K., LANIN, V. A., AND TIKHONOVA, Z. T. [Formation of Methane in the Preparation of Water Gas From Peat Coke.] Jour. Chem. Ind. (U. S. S. R.), vol. 11, 1934, No. 7, pp. 50–52; Chem. Abs., vol. 29, 1935, p. 321.

CH_4 is formed from CO and H_2 owing to the great catalytic activity of the peat coke.

1790. KLING, A. [Production of Fatty Acids From Paraffins.] Parfumerie, vol. 1, 1943, pp. 185–188, 213–216; Chem. Abs., vol. 40, 1946, p. 5269.

Address briefly reviewing the general processes for synthesizing paraffins and for their controlled oxidation for the production of industrial, and even edible, fatty acids. A major part of the address is devoted to the Fischer-Tropsch process and to the work of Arditti.

KLINGER, P. See abs. 1498.

1791. KLYUKVIN, N. A. AND KLYUKVINA, S. S. [Conversion of Methane. I.] Jour. Chem. Ind., U. S. S. R., vol. 7, 1930, pp. 743–752; Chem. Abs., vol. 25, 1931, p. 4520.

Investigation deals with conversion of CH_4, industrially available in great quantities as a waste product, into commercial products. Catalytic conversion of CH_4 can be used industrially for the production of H_2. CH_4 and mixtures of CH_4 with CO_2 and with H_2O were passed through porcelain tubes 50 cm. long and 16 mm. in diameter, or Fe tubes 100 cm. long and 22 mm. in diameter heated in an electric oven 28 cm. long. The temperature was measured with a pyrometer provided with a Pt thermocouple and inserted in a quartz tube. The gases were conducted at the rate of 3,000 cc./hr., or 38 sec. of contact. With reduced NiO as catalyst in

a porcelain tube only 1.6% CH_4 remained unchanged at 850°, while without a catalyst 69.8% at 850° and 57.2% of CH_4 at 1,000° were recovered. The gas contained also H_2 94.3 and N_2 4.1% and showed 99.6% increase in vol. The thermal decomposition of CH_4 may be complicated by side reactions with formation of CO and CO_2, and, when no Ni is used, with unsaturated compounds. A mixture of CH_4 and CO_2 (1 : 1) produced with Ni at 1,000° 97.6% conversion (95% increase in vol.); the reaction is based on the formula: $CH_4 + CO_2 = 2 CO + 2 H_2$. The gas was composed of CO 47, H_2 48.6, N_2 2.6% and no byproducts. The formation of CO begins at 700°. An addition of Al_2O_3 to Ni (2 : 1) does not change the general character of the reaction but retards somewhat the progress of conversion. This experiment repeated without a catalyst gave in a porcelain tube at 1,000° only 43% conversion of CH_4, and in Fe tubes 58%. Under equal conditions, the conversion of CH_4 is in direct proportion to the speed with which the gas is passed through the reaction tube, and at the velocity of 9 l./hr., instead of 3 l./hr., is reduced by 10%.

1792. ——. [Conversion of Methane. II.] Jour. Chem. Ind., U. S. S. R., vol. 7, 1930, pp. 877–885; Chem. Abs., vol. 25, 1931, pp. 4520–4521.

Conversion of CH_4 with H_2O was carried out in an Fe tube 100 cm. long and 22 mm. in diameter. As catalysts reduced NiO (16 gm.) and NiO (24 gm.) were used. The gas mixture consisted of 1 vol. of CH_4 and 4 vol. of steam and was passed with a velocity of 6 liter/hr. The conversion is based on the formula $CH_4 + H_2O = CO + 3H_2$, which at low temperature may be modified to: $CH_4 + 2H_2O = CO_2 + 4H_2$, while the interaction of the reaction products may be as follows: $CH_4 + CO_2 = 2CO + 2H_2$ and $H_2O + CO = CO_2 + H_2$, all of which is substantiated by the composition of the resulting gas. The best result obtained is 98.4% conversion of CH_4 with 218% increase in volume, the gas containing CO_2 5.8, CO 12.6, H_2 80, O_2 0.4, N_2 0.7, CH_4 0.5% and no unsaturated compounds. A substitution even in part of Al_2O_3 or reduced Fe for Ni produced unsatisfactory results. Activated vegetable C gives 100% conversion of CH_4 at 800° with 142% increase in volume, while the respective figures for reduced Ni at 800° are 33.3 and 100%. At lower temperature (500°–700°) both catalysts give about equal conversion of CH_4, but the quantity of gases obtained is higher with C; this indicates that the conversion of CH_4 is accompanied by decomposition of water: $C + 2H_2O \rightarrow CO_2 + 2H_2$. At 700° the resulting gas mixtures contain 1.2% of CO_2 with Ni and 10.4% with C. It must be noted, however, that the increase in vol. is 142% with C and 218% with Ni. The conversion of CH_4 with C catalyst without H_2O results at 800° in 26.9% and at 900°–950° in 100% conversion of CH_4 with 100% increase in vol. The gas is of exceptional purity, containing CO_2 0.2, CO 0.8, H_2 93.1, N_2 5.9% and no O_2, CH_4 or unsaturated compounds. To investigate more closely the catalytic action of activated C in the thermal conversion of CH_4, the last 2 experiments were repeated with C in porcelain tubes instead of Fe tubes, thereby eliminating any possibility of the catalytic action by Fe. Since the velocity of the gas was 6 l./hr. instead of 3 l./hr. as in the experiments with Ni, it can be concluded from the results that C is a less active catalyst than Ni. With Ni the reaction begins at 300° and reaches a complete conversion of CH_4 at 850°, while with C it starts only at 500°–600°, and ends with only 62.4% of conversion at 1,000°. The test with inactivated birch C under these conditions produced at 1,000° 47.1% conversion of CH_4 in a porcelain tube, and 100% conversion with 100% increase in vol. at 900° when conducted in an Fe tube; that is, equal in its activity to activated C. From 27 gm. of the C used 26.8 gm. were recovered after 8

experiments. A catalyst containing 9 gm. of inactivated birch C and 72 gm. of Fe filings produced in a porcelain tube at 1,000° 100% conversion of CH_4 with 100% increase in vol., the gas containing H_2 97.5, N_2 2.5% and no other products. The results are similar to those obtained with Ni and with C in an Fe tube. No decrease in weight of the catalyst was observed after 9 experiments.

1793. ———. [Chemical Treatment of Natural Gases. I.] Prirodnuie Gazui, vol. 2, 1931, pp. 91–128; Chem. Abs., vol. 26, 1932, p. 1416.

CH_4 containing 8% N_2 was passed through a porcelain tube in the presence of reduced Ni and heated at various temperatures; the highest conversion to H_2, amounting to 94.3%, was attained at 850°, the balance being 1.6% CH_4 and 4.1% N_2, while under the above condition with a temperature of 1,000° 57.2% of CH_4 still remained unchanged when the reaction was carried out without a catalyst. Equal volumes of CH_4 and CO_2 require a 100° higher temperature. In the conversion of CH_4 and H_2O vapor in the presence of a mixture of Ni and NiO catalysts the highest yields (increase of volume by 205%) were obtained at 900° and a $CH_4 : H_2O$ ratio of 1 : 4 and 1 : 5. When activated wood charcoal was substituted for the Ni catalyst, a complete conversion was obtained at 750°–800°, but the yield of H_2 amounted to only 55.9%, while 37.7% CO was present in the final gas mixture. This is probably due to the reaction $C+H_2O \rightarrow CO+H_2$, favored by temperatures exceeding 750°. Conclusion: The conversion of gases containing CH_4 is commercially feasible. The process temperature is of the magnitude of 800°–950°. Reduced Ni may be used as catalyst. Semicoke prepared from brown coal as well as coke from hard coal are catalysts equivalent to Ni. An excess of H_2O favors the formation of H_2. The thermal decomposition of CH_4 in the presence of water vapors is insignificant above 800°, and a complete conversion is obtained at about 900°.

1794. ———. [Preparation of Mixtures of Carbon Monoxide and Hydrogen for the Synthesis of Alcohol.] Natural Gases, U. S. S. R., vol. 8, 1934, pp. 52–58; Chem. Abs., vol. 31, 1937, p. 3642.

Of 16 Ni catalysts tested, Ni–Th–Mg on kieselguhr and Ni–Fe on kieselguhr were best. In the presence of Ni–Fe on kieselguhr, with an excess of water vapor ($CH_4 : H_2 = 1 : 1.5$) and a concentrate of natural gas (CH_4 60 and N_2 40%), containing CH_4 91, and N_2 9%, yielded at 750° CO_2, 1, CO, 20, and H_2 75%. The gas mixture obtained used in alcohol synthesis in the Patart apparatus at 350° under an initial pressure of 150–125 atm., in the presence of a Zn–C catalyst and a velocity of 18,000 l./hr., yielded 113–187 cc. of condensate boiling at 65°–75°, 17.9–18.8; 75°–85°, 69.9–65.7; and 85°–95°, 2.2–2.6%. Activation of the Fe catalyst with a 1% admixture of Ni promotes formation of water gas at 900°, whereas a 5% admixture of Ni reduces the CO formed to C. Activation of the catalyst with a 5% admixture of Mg yields satisfactory results at 900°.

1795. KLYUKVIN, N. A., AND VOL'NOV, Y. N. [Synthetic Hydrocarbons From Water Gas.] Khim. Tverdogo Topliva, vol. 4, 1933, pp. 355–362; Chem. Zentralb., 1934, II, p. 3464; Chem. Abs., vol. 28, 1934, p. 6279.

Catalysts Ni–Th, Ni–Th–Hg, and Ni–Mg were best for the production of gasoline from CO and H_2, yielding under the most favorable conditions 0.1 gm. of gasoline per l. gas passed, that is, 30–40% on the converted CO, this yield being raised to 98–100% on recycling. By the proper selection of the catalysts and the process conditions, a product high in unsaturated compounds can be obtained. 26 refs.

1796. KLYUKVIN, N. A., VOL'NOV, Y. N. AND KARPINSKII, M. N. [Ethanol Synthesis. I.] Khim. Tverdogo

Topliva, vol. 3, 1932, pp. 829–837; Chem. Abs., vol. 28, 1934, p. 5806.

Feasibility of various methods for the preparation of EtOH is discussed. The experiments were carried out with a gas containing CO 33.4, H_2 66.2 and CO_2 0.4%. After the experiments the composition of the gas was changed; it contained CO_2 up to 12, CH_4 11, CO about 33.4 and the amount of H_2 decreased to 45–50%. The condensate contained fractions boiling 60°–70°, 76°–80° and above 80°. The highest yield, 39%, of EtOH was attained at 320°–330°, 120 atm. and in the presence of ZnO : CoO : : 3 : 1, catalysts. A series of alcohols from Me to Am were traced in addition to EtOH. The experiments are described and the effect of changes in the experimental conditions is shown on diagrams.

KLYUKVINA, S. S. *See* abs. 1791, 1792, 1793, 1794.

KNAPP, B. *See* abs. 166.

1797. KNEULE, F. [Tendency to Carbonization of Diesel Fuel.] Ztschr. Ver. deut. Ing., vol. 86, 1942, pp. 76–78; Brennstoff-Chem., vol. 23, p. 285; Chem. Abs., vol. 37, 1943, p. 3903.

Experiments showed that the Conradson carbonization test is a reliable indication of the tendency of a fuel to deposit C on the fuel-inlet nozzles. Addition of relatively small amounts of Fischer-Tropsch products can lower the coking tendency of many fuels.

——— *See* abs. 3093.

1798. KNIEL, L. Propane Recovery by Absorption. Petrol. Processing, vol. 3, No. 11, 1948, pp. 1066–1072; Petrol. Refiner, vol. 27, No. 11, 1948, pp. 588–593.

Presented at meeting of the California Natural Gasoline Association. Increased extraction of propane in the required purity in absorption-gasoline plants may be achieved through changes in the fractionating absorber and its important adjuncts, the gas cooler and partial condenser. Design formulas are presented for the absorber, for the determination of liquid and vapor traffic, key temperatures, and other factors that relate to retention in the absorber and to rejection in the stripper with overall recovery. Plant design based on the formulas is applied to the recovery of 90% propane from a wet gas of specified composition, as an example. Product costs are shown lower than in most conventional plants handling an equal volume of gas and recovering gasoline and butanes only. The direct cost of production is calculated at $0.705 per gal. of total liquid products recovered.

——— *See* abs. 3227.

1799. KOBAYASHI, K. Production Methods of Synthetic Fuels and Oils. Trans. World Power Conf., Tokyo Sectional Meeting, vol. 1, 1929, pp. 574–576; Chem. Abs., vol. 26, 1932, p. 2298.

1800. ———. Recent Investigations on the Synthesis of Petroleum. Jour. Fuel Soc. Japan, vol. 12, 1933, pp. 436–446; Chem. Abs., vol. 27, 1933, p. 3808.

Brief review of progress in Japan.

1801. KOBAYASHI, K. AND YAMAMOTO, K. Synthesis of Petroleum Hydrocarbons From Hydrogen and Carbon Monoxide at Ordinary Pressure. I. Jour. Soc. Chem. Ind. (Japan), vol. 32, 1929, p. 54; Suppl. 32, 1929, p. 23B; Chem. Abs., vol. 23, 1929, p. 5035.

Experiments are described in which petroleum hydrocarbons were obtained by passing a mixture of 3 vol. of H_2 and 2 vol. of CO over a catalyst consisting of Co, Cu and Mn at about 300° under atmospheric pressure.

1802. KOBAYASHI, K., YAMAMOTO, K., AND ISHIKAWA, H. Synthesis of Petroleum Hydrocarbons From Hydrogen and Carbon Monoxide at Ordinary Pressure. II. Mem. Faculty Sci. Eng. Waseda Univ. (Tokyo), No. 7, 1930, pp. 26–27; Chem. Abs., vol. 25, 1931, p. 2840.

Nine catalysts composed of Co, MnO and Cu were used in the synthesis of oil from CO and H_2. Active C formed from the decomposition of the CO is considered the basic material for subsequent hydrogenation and polymerization to oils. CH_4 was formed simultaneously.

1803. ———. Synthetic Petroleum From Carbon Monoxide and Hydrogen. Jour. Fuel Soc. Japan, vol. 9, 1930, p. 40.

Paper presented at the 33d annual meeting of the Society of Chemical Industry, Japan. In the synthesis of petroleum, it is necessary, first of all, to explain the mechanism of the reaction, which can be divided into the following 4 stages: (1) Decomposition of CO into CO_2 and C, the latter in a nascent state; (2) the reaction between CO and H_2 with CH_4 and H_2O as the products; (3) production of C_2H_4 and C_2H_2 from C liberated in stage 1; (4) condensation of C_2H_4 and C_2H_2 into petroleum. To obtain the maximum yield of petroleum, it is important to accelerate reactions 1 and 3 and depress 2 as far as possible. For this purpose, the reactions must be carried out separately in the production of C_2H_4 and C_2H_2 on the one hand and the condensation of those products on the other.

KOBE, K. A. *See* abs. 2759.

1804. KOBOZEV, N. I. [Mechanism of the Inhibiting Effect of Promoters on the Reduction of Iron-Ammonia Catalysts.] Acta Physicochim. U. R. S. S., vol. 4, 1936, pp. 829–840; Chem. Abs., vol. 30, 1936, p. 7987.

Theoretical discussion based on the results of Natanson (abs. 2370) and Dubrovskaya and Kobozev (abs. 749).

1805. ———. [Mechanism of the Retarding Effect of Promoters on the Reduction of Iron-Ammonia Catalysts.] Jour. Phys. Chem. (U. S. S. R.), vol. 8, 1936, pp. 226–233; Chem. Abs., vol. 31, 1937, p. 1559.

Data are given for the retarding effects of K_2O, BeO, KF, and Al_2O_3 on the reduction of Fe_2O_3 by H_2 and of MgO on that of FeO. Promoter action of the catalyst results when the added substance is surface-active and reduces the rate of reduction of the Fe oxide.

——— *See* abs. 749.

1806. KOBOZEV, N. I., EROFEEV, B. V., KAVERIN, I. B., AND BOGOYAVLENSKAYA, A. N. [Mechanism of the Promotion Action of Iron Ammonia Catalysts.] Acta Physiochim. U. R. S. S., vol. 1, 1934, pp. 483–492; Chem. Abs., vol. 29, 1935, p. 7774.

Promoting action of Al_2O_3 and MgO on FeO was studied from the viewpoint of mixed crystals between the promoter and the initial Fe oxide. The formation of mixed crystals is not enough, in itself, to cause the promoting action. It was proposed that it was necessary for a promoter to be surface-active with regard to the initial mass of the catalyst. A pronounced difference between the surface tension of Fe_3O_4 and $Fe_3O_4+Al_2O_3$ and an absence of such a difference between FeO and FeO+MgO as confirmed by the catalytic activity of Fe reduced from these oxides was experimentally shown.

1807. KOCH, H. [Synthesis of Benzine From Carbon Monoxide and Hydrogen Under Atmospheric Pressure by the Method of F. Fischer and H. Tropsch.] Glückauf, vol. 71, 1935, pp. 85–90; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 577–587; Chem. Abs., vol. 29, 1935, p. 6401.

Fundamental principles of the synthesis with reference to mechanism of reactions, preparation of catalysts, and reacting gases and properties of primary and secondary products. The best gas mix contained 29% CO and 58% H_2, which with a Co catalyst yielded

an oil, 62% boiling at 30°–200°, containing 30% olefins. Other products were 4% boiling at <30°, 23% boiling at >200°, and 14% solid paraffin. A Co–Th catalyst precipitated on kieselguhr gave a yield of 110 gm. of oil for 60 days, after which the efficiency began to decrease. The motor-spirit fraction must be rendered anti-knocking, for example, by blending with C_6H_6. Heavy oils lend themselves to preparation of synthetic alcohols and motor spirit through cracking and subsequent treatment of cracked residues. Lubricating oils of superior quality are prepared from the olefins by condensation in the presence of $AlCl_3$ or from the paraffins by chlorination and condensation with aromatic hydrocarbons, for example, xylene. The mechanism of the reactions by which liquid hydrocarbons are formed involves formation of metallic carbides; these react with H_2, forming CH_2, which condenses.

1808. ———. [Synthetic Lubricating Oils.] Ztschr. Ver. deut. Ing., vol. 80, 1936, pp. 49–50; Coal Carbonisation, vol. 2, 1936, p. 63; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 588–592; Mech. Eng., vol. 58, 1936, pp. 248–249; Chem. Abs., vol. 30, 1936, p. 2741.

Good yield of lubricating oil can be obtained by polymerization of the olefin hydrocarbons in the Kogasin product of the Fischer-Tropsch synthesis. It is desirable that the monoolefin content should be as high as possible and can be brought about by using a 1 : 1 ratio of CO to H_2 instead of the usual 1 : 2 ratio whereby a Kogasin is obtained with 50% of reactive olefins. Polymerization is effected by $AlCl_3$ catalyst in about 8 hr. at 100° C. Synthetic lubricants from the olefin fractons of boiling point 125°–250° C. are equal in viscosity to the best Pennsylvania oils, their specific gravity is only 0.84–0.85, and their coking tendency is very low. They are quite free from S and have very low setting points (−30° C. for an aviation lubricant of 123 Engler viscosity at 20° C.). With the present development of the process, the yield of thick oils is about 60% of the weight of olefins treated; most of the remaining 40% is converted to comparatively thin oils, which can be combined with the gas-oil fraction. For a further increase in total yield, the paraffin hydrocarbons of the Kogasin can be processed by chlorination and catalysis, yielding another series of lubricating oils of excellent quality.

1809. ———. [Some Properties of Synthetic Lubricants From Kogasin.] Brennstoff-Chem., vol. 18, 1937, pp. 121–127; British Chem. Abs., 1937, B, p. 408; Chem. Abs., vol. 32, 1938, p. 8756.

Previous work reviewed briefly. Essential differences from petroleum lubricants such as higher H_2 content and lower specific gravity are discussed. Various Kogasin products, a number of American and European petroleum products, and a polymerization product of 2-pentene are compared for specific gravity, average molecular weight, kinematic viscosity at 20° and 50°, and viscosity-temperature index. The first named with viscosity-temperature characteristics improved over those previously reported are residual distillation fractions boiling >200° and 250° at 15 mm. Hg. The 2-pentene product gave a very steep viscosity-temperature curve. At corresponding viscosities, Kogasin molecular weights are higher than those of the petroleum products. A wide range, 355–1,029, of average molecular weights is encountered. The Wijs I numbers increase with viscosity and for the better lubricating fractions are similar to those of petroleum products. Mild and strong hydrogenations of Kogasin lubricants with Co and Ni catalysts beginning with 100- atm. at 180° show corresponding decrease in I number with increase in absolute viscosity but with slight increase in viscosity-temperature index. Comparisons of two Pennsylvania oils, three Kogasin oils (one hydrogenated), and a commercial transformer

oil for aging effects, light, and air treatment, showed sludge in the last after 8 days, considerable sludge in the winter-grade motor oil, but none in the summer-grade or Kogasin products even after 8 mo. Acid and saponification numbers show somewhat less increase in the synthetic products. Aging was greatly accelerated in the parallel tests by the presence of H_2O, even the summer oil formed sludge. Asphalt could not be precipitated from aged Kogasin oils by addition of petroleum ether, in contrast to the natural oils; S is absent in the former. Subjected to the British Air Ministry test (2 6-hr. periods at 200° in air current) the aged Kogasin oils remained clear but colored, free from asphalt, doubled in viscosity (fourfold for the hydrogenated oil). In contrast, the aged petroleum oils became darker, cloudy, contained much asphalt, and increased to 8 times in viscosity. For both types of oils, the viscosity-temperature indexes increased slightly, the average molecular weight increased 10%, and Conradson C increased but remained lower in the Kogasin oils. Hydrogenation at 190°-200° with Ni catalyst after aging by this method restored the original properties of the Kogasin products. Practical motor tests showed 10% increase in viscosity after 3,800 km. acid and saponification numbers increased to 2.5 times, Conradson C increased from 0.125 to 0.22%, viscosity-temperature index changed from 1.85 to 1.83. Tests of low-viscosity oils, as transformer oils, show no depreciation in properties, the original Kogasin oil falling far within tolerances as to saponification and acid numbers, H_2SO_4 test, and with electrical breakdown of 180 kv. per cm. 15 refs.

1810. ———. [Newer Investigations of Lubricating Oils Prepared From the Synthesis Product (Kogasin) of the Fischer-Tropsch Process.] Brennstoff-Chem., vol. 19, 1938, pp. 337–343; Proc. Pure Applied Chem., Rome, 10th Intern. Congr., 1938: British Chem. Abs., 1938, B, p. 1385; Chem. Abs., vol. 32, 1938, p. 9466.

Viscometric properties, chemical composition, aging characteristics, influence of hydrogenation, and behavior in use of monoolefins prepared from Kogasin are described and discussed with comparative data and references. More recent work shows the dependence of the viscosity-temperature behavior not only on the boiling range of the Kogasin fractions used in preparation of the oils, but on the olefin content of the fractions. Studies in determination of the I number of Kogasin lubricants by various methods show the importance of controlling time, concentration, and excess reagent in the tests. Ring analyses show approximately 1 naphthene ring per mol. regardless of viscosity-temperature characteristics. Similarly, extraction with acetone indicates that the proportion of the ring is the same in fractions of all viscosities. Aging tests of oil for transformer use by the method of Weiss and Salomon showed no sludge formation in 11 days. Exhaustive hydrogenation increased oil stability to light and air progressively to low acid and saponification numbers after 6-mo. storage tests.

1811. ———. [Artificial Production of Lubricating Oils.] Arch. Eisenhüttenw., vol. 12, 1939, pp. 533–537; Umschau, vol. 43, 1939, pp. 195–197; Chem. Abs., vol. 33, 1939, p. 5639.

Trend to produce more and more synthetic lubricating oils instead of using the natural oils with their widely varying properties is justified by the much greater uniformity that can be obtained in the synthetic oils. The various methods of producing synthetic oils are discussed. 10 refs.

1812. ———. [Catalytic Aromatization of Aliphatic Hydrocarbons. Literature Review and Verification.] Brennstoff-Chem., vol. 20, 1939, pp. 1–9; Chem. Abs., vol. 33, 1939, p. 9280.

Procedure of Italian Patents 351,078 and 352,747 was used in treating the C_7 Kogasin fraction at 500° with V and Cr oxides on Al_2O_3 for catalysts. Treatment of the fraction boiling at 92°–95° and containing 68% heptene was attempted at 400°–530°; toluene was formed as the main constituent in an aromatic yield of 55% with 1 pass. Dehydration, cyclization, and cracking also occurred, and the action of their products required frequent reoxidation of the catalyst. In comparison, the reaction yield was much smaller when platinized C at 310°–350° was used. With gasoline boiling >100° and prepared by the activated-C process, d. was increased from 0.710 to 0.742 and n_D from 1.404 to 1.422 without the formation of low-boiling hydrocarbons in 5 sec. contact time at 520° with V oxide on Al_2O_3. From a Kogasin fraction boiling 150°–300° passed over Cr oxide on Al_2O_3 for 3–4 sec. at 500°–510°, 15% low-boiling material was produced in which benzene, toluene, xylene, and PhEt were identified. Gaseous products, depending upon the conditions and starting material, consisted of 5–10% unsaturated and 10–20% saturated compounds. 10 refs.

1813. ———. [Synthetic Lubricating Oil.] Umschau, vol. 43, 1939, pp. 195–197; Arch. Eisenhüttenw., vol. 12, 1939, pp. 533–537; Chem. Abs., vol. 33, 1939, p. 7086.

Discussion of what has been realized to date commercially in the synthesis of improved lubricating oils from raw materials, such as coal, animal oils, and petroleum products.

1814. ———. [Alkylation of Aliphatic Hydrocarbons, Particularly With Regard to Kogasin.] Reichsamt Wirtschaftsausbau, Prüf-Nr. 102, 1940, pp. 49–57; PB 52,004; Chem. Abs., vol. 41, 1947, p. 6698.

By alkylation in the presence of anhydrous HF the products of Kogasin (heavy oil from the Fischer-Tropsch process) synthesis can be converted into high-antiknock fuels similar to isooctane. The HF catalyst gives few side reactions, has a long life, and when activated by BF_3, also can be used for the conversion of C_2H_4 or ethylenic mixtures. Fractions of Kogasin not useful elsewhere are either isomerized and split with $AlCl_3$ or pyrolized, to give an olefin mixture suitable for the alkylation reaction.

1815. ———. [Quantitative Separations of Hydrocarbons by Distillation at Various Temperatures and Separation of Olefins and Paraffins.] Reichsamt Wirtschaftsausbau, Prüf-Nr. 48, 1940, pp. 93–102, PB 52,003; Chem. Abs., vol. 41, 1947, p. 6492.

Separation and identification of some of the components of Kogasin are described. For studying the lower hydrocarbons, a low-temperature column was designed that consisted of a 6-m. spiral of glass tubing of 5 mm. inside diameter surrounded by a vacuum jacket. The head of this column works on the thermo-siphoning principle. With a test mixture of n-heptane and methylcyclohexane, this column showed 20 theoretical plates. A chart of the separation of C_5H_8, n- and iso-C_4H_{10}, and iso-C_5H_{12}, is shown. A high-temperature column was developed in which a heated oil was circulated around the column to maintain adiabatic conditions. A review of the results obtained in number-methods for olefins is described. The Kaufmann and Gross-Oetringhaus thiocyanogen method using CCl_4 gave the best results for the 5 olefin types. The Hg(OAc)2-MeOH method was used for separating olefins from paraffins. An olefin-paraffin mixture was extracted with Hg(OAc)$_2$-MeOH reagent, and the paraffin was removed from the reaction mixture by reduced-pressure distillation. The olefins were recovered in pure form by hydrolyzing the Hg(OAc)$_2$ olefin complex with a strong mineral acid such as HCl. Of the paraffins in a lower Kogasin fraction, 2-methyl-butane, n-C_5H_{12}, 2-methylpentane, 3-methylpentane,

n-C_6H_{14}, 2-methylhexane, 3-methylhexane, and n-C_7H_{16} have been isolated. Of the monoolefins 3-methyl-1-butene, 1-pentene, cis-and trans-2-pentene, 3-methyl, 1-pentene, 4-methyl, 1-pentene, 1-hexene, cis-and trans-2-hexene, 3-methyl-1-hexene, 5-methyl-1-hexene, 4-methyl-1-hexene, 1-heptene, and cis-and trans-2-heptene have been isolated.

1816. ———. [Decomposition of Synthetic Paraffin by Hydrogenation.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 9.

Paper presented at the 1949 meeting of the Deutsche Gesellschaft Mineralölwissenschaft u. Kohlechemie. Synthesis paraffin was subjected in a stream of water at about 200° to selective demethylation. In the gasoline fractions obtained from the decomposition products, the degree of branching was ascertained, and conclusions were drawn as to the content of isohydrocarbons in the synthesis paraffins.

1817. ———. [Development of the Fischer-Tropsch Hydrocarbon Synthesis Process.] Chem.-Ztg., vol. 74, No. 8, 1950, pp. 103–106.

Reviews progress.

See abs. 983, 984, 985, 986, 1032, 1033, 1034, 1048, 1362, 3458.

1818. KOCH, H., AND BILLIG, R. [Investigation of the Solid Paraffin Hydrocarbons Produced in the Benzine Synthesis of F. Fischer and H. Tropsch Atmospheric Pressure Synthesis.] Brennstoff-Chem., vol. 21, 1940, pp. 157–167; Chem. Abs., vol. 35, 1941, p. 3803.

Previous work reviewed briefly. By use of apparatus previously described, the solid products recovered with the liquid hydrocarbons in the train beyond the catalyst tube and the high-melting ceresins extracted from the catalyst itself after prolonged use have been investigated. Similarly, quantitative relations between molecular weight and melting point of products solid at room temperature, establishment of isoparaffins by physical and chemical data, and conversion of fractionated extracts into lubricants have been studied. Appreciable increase of extracted ceresin, accompanied by decreased yield of other products and the elevation of average boiling range of condensates, followed the alkalization of the Co-Th on kieselguhr catalyst with 0.25–2% Na_2CO_3 and 0.5–1% K_2CO_3 in 4-l.-per-hr. tests with 29% CO–59% H_2 gas mixtures at 190°–200°. As much as 50% more solid paraffins were found in the fraction boiling >300°. Paraffin precipitation was carried out over the range +5° to −20°, with 1:5 to 1:100 oil:solvent ratios. Between certain limits, the amounts of solid paraffins decreased steadily with increasing melting point. The regularity of the relation was found also in products of Fe-Cu and technical-scale syntheses. By fractional extraction of a Kogasin paraffin with 3:2 ether-alcohol mixture and of the ceresins with ether, 13 and 15 close fractions were obtained, respectively. The synthetic ceresin and several fractions thereof, treated with HSO_3Cl, decreased 1.3°–1.9° and increased 1°, respectively, in melting point, and their average molecular weights increased by 10–40. The reaction was preferential for isoparaffins. Hydrogenation under 80 atm. pressure around 190° with Ni catalyst gave colorless products, increases of 0.0002 in n_D, and 1° in melting point. In solidification curves, the ceresin fractions exhibited definite points of heat of crystallization as compared to the perfectly smooth-cooling curve of the whole ceresin. 15 refs.

1819. ———. [Preparation of Lubricants From Solid Paraffin Hydrocarbons of the Fischer-Tropsch Atmospheric Pressure Synthesis by Way of Their Olefinic Cracked Distillates.] Brennstoff-Chem., vol. 21, 1940, pp. 169–177; Chem. Abs., vol. 35, 1941, p. 3803.

Method used by Sullivan and others, with natural solid and paraffin-wax fractions of petroleum, has been applied to fractional extracts from Kogasin paraffin and from synthetic ceresin. Repeated passes gave 40–50% yields of nearly pure olefins boiling >250°, with 35–45% cracked gas containing 60% of unsaturated hydrocarbons. The distillate boiling >250° was converted to lubricants with 5% anhydrous $AlCl_3$ in a 7-hr. reaction to 60°, with 65–75% yields of oils of good viscosity-temperature relations, poles of 1.57–1.83 abs. viscosity of 240–820 centistokes° or 32°–108° E. Yield of a diesel oil was 5–14%. However, close fractions obtained from the cracked distillates of the ceresins produced lubricants whose viscosity behavior depended upon the boiling ranges of the corresponding fractions. Viscosity poles decreased with increasing boiling range, for example, for the 230°–250° fraction, the lubricant pole was 1.31. Lubricants from 5 of these fractions were hydrogenated with Ni catalyst at 250°–260° at 80 atm. subsequently, and complete physical examination generally showed no appreciable change in viscosity-temperature relation. However, viscosity increased around 10% without great change in average molecular weight n_D averaged 0.0004 lower, solid point increased 1°–2°, and aniline point increased 4°–5°. Ring analyses showed 1.51–2.88 naphthalene rings per mol. and on the basis of molecular weight were parallel to viscosity poles. 11 refs.

1820. KOCH, H., AND GILFERT, W. [Synthesis of Lubricating Oils From Olefins of Kogasin. I.] Brennstoff-Chem., vol. 20, 1939, pp. 413–420; Chem. Abs., vol. 34, 1940, p. 8240.

Kogasin fraction was treated with 5% (calculated on olefin content) of anhydrous $AlCl_3$ with vigorous stirring (1 hr. at 0°, 3 hr. warming to room temperature, 1 hr. heating to 50°, 3 hr. at 50°). The polymerization product was separated from the $AlCl_3$ compound; treated with fuller's earth and freed from the lower boiling constituents by distillation to 200° per 15 mm. Fractions from (I) Kogasin from water gas (1CO:1H$_2$) and from (II) Kogasin from synthesis gas (1CO:2H$_2$) were used. Fractions from (I) corresponding approximately with C_5, C_6 and C_7 hydrocarbons, respectively (olefin content 70–75%), gave about 65% (calculated on olefin content) of lubricating oil having a viscosity of 1,110–1,550 centistokes at 20° and viscosity-pole heights of 1.88–2.33; the corresponding fractions from (II) (olefin content 43–55%) gave lower yields (37–55%) of oils having a viscosity of 473–585 centistokes at 20° and viscosity-pole heights of 2.23–3.10. The lower yields from (II) were due, not to the lower olefin content of the starting material, but to a difference in constitution of the olefins. When the olefin content of (I) was reduced by partial hydrogenation lower yields of an inferior oil were produced by polymerization of the remaining olefins. The C_6 and C_7 fractions were refractionated into narrow cuts, from each of which a lubricating oil was synthesized. The properties of the products varied considerably with the boiling-point of the starting material; for example, the viscosity of the oils from the C_7 fractions varied from 22,777 (from fraction 57.0°–61.0°) to 476 (from fraction 67.5°–9.0°) centistokes at 20°; the flattest viscosity-temperature curve (viscosity-pole height 1.77) was given by oil from the fraction 63.0°–3.5° (principally 1-hexene) and the steepest (viscosity-pole height 2.53) by the oil from the fraction 67.5–9.0 (2-hexene). The products from the C_7 fractions showed similar but somewhat less marked variations in properties. In neither case was there any apparent relation between the absolute viscosity of the oils and the viscosity-pole height. The mean molecular weight of the lubricating oils varied 550–1,240.

1821. ———. [Synthesis of Lubricating Oils From Olefins of Kogasin. II.] Brennstoff-Chem., vol. 21, 1940, pp. 1–7; Chem. Abs., vol. 34, 1940, p. 8240.

By lowering the temperature of polymerization of a C_3 Kogasin fraction (in presence of anhydrous $AlCl_3$) from 20° to 0° a more viscous lubricating oil was obtained; its viscosity-temperature behavior was not appreciably affected. At —80° no polymerization occurred. All the lubricating oils produced by polymerization of Kogasin fractions had 1 double bond per mol. Saturation of this bond by hydrogenation caused some increase in the viscosity of the oil, but had little effect on the viscosity-temperature coefficient. Examination of the oils by Waterman's method indicated the presence of 1 naphthene ring per mol., even for oils of considerably different viscosity-pole heights. The relation between viscosity and the mean molecular weight of the oils is discussed; in this respect some differences are observed between the synthetic oils and petroleum lubricating oils.

1822. ———. [Breaking Down and Building Up of Hydrocarbons Under Hydrogenating Conditions Over the Cobalt Catalyst Used in Fischer-Tropsch Syntheses.] Brennstoff-Chem., vol. 30, 1949, pp. 213–218; Chem. Zentralb., 1950 I, p. 1302; Chem. Abs., vol. 43, 1949, p. 7663.

Various hydrocarbons in vapor form mixed with H_2 and CH_4 were recirculated at 200° over a reduced Co catalyst used for Fischer-Tropsch syntheses. The paraffin hydrocarbons n-C_6H_{14}, n-C_7H_{16}, n-C_8H_{18}, and 2-methylpentane in a current of H_2 were broken down by demethylation, about half of the hydrocarbon being converted. In addition to shortening the C chain, there was also a distinct building up to the next higher homolog. Isomerization also occurred to a slight extent, and some aromatization occurred with 2-methylpentane. With n-C_6H_{14} mixed with the circulating gas containing CH_4, considerable chain lengthening to C_7H_{16} took place, presumably because of combination with CH_4. In CH_4 without H_2, the n-C_6H_{14} remained unchanged. Toluene was formed to a surprising extent by the conversion of cyclohexane in a stream of H_2. At the same time, C_6H_6 was formed by dehydrogenation and cyclopentane, by way of isomerization, to methylcyclopentane followed by demethylation. Benzene reacted with H_2 to form toluene, but this conversion was relatively slow. No increase of the toluene yield was produced by adding CH_4 to the circulating gas.

1823. Koch, H., and Hilberath, F. [Literature Review and Comparative Investigations of Methods for Determining the Iodine Number of Hydrocarbons.] Brennstoff-Chem., vol. 21, 1940, pp. 185–194; Chem. Abs., vol. 35, 1941, p. 7319.

Reviews 62 papers published since 1884. The Wijs, Kaufmann, and iodo-thiocyanate methods and the procedures of Hanus, Francis, and Grosse-Oetringhaus have been compared for 17 simple olefin hydrocarbons. For the exact determination of the I number of aliphatic monoolefins and hydrocarbon mixtures, the methods of Kaufmann and Grosse-Oetringhaus alone are suitable. For approximations, the KBr-KBO_3 method of Francis is suitable. The use of the Wijs, Hanus, and Kaufmann methods involves large substitution errors with tertiary or ditertiary olefins. These 3 methods can be used with olefins not branched at the double bond, as with the Kogasins. No general conclusions were reached for the determination of cyclic monoolefins because of few data: Cyclopentene and cyclohexene can be analyzed by the methods named, but side reactions were observed with certain unsaturated cyclic terpenes. Conjugated double bonds in dienes can be considered as having the I consumption of single double bonds with the iodo-thiocyanate, Wijs, and Hanus methods. On the other hand, the method

of Francis, as modified by Cortese, produces complete saturation, and the method can be used in combination with the other methods to determine the content of conjugated double bonds in mixtures by difference. Few tests were made with acetylenes; the methods of Wijs and Hanus give 50% of the theoretical I-consumption; the method of Lucas and Pressman gives complete saturation in the absence of substitutable olefins. With synthetic Kogasin lubricating oils, the suitability of the iodo-thiocyanate method for the exact determination of double bonds and the Wijs method (limited to 2–3 min. reaction time) for approximations was shown.

1824. ———. [Suitable Apparatus for Fractional Distillation at Low Temperature.] Brennstoff-Chem., vol. 21, 1940, pp. 197–203; Chem. Abs., vol. 35, 1941, p. 7239.

Previously proposed apparatus are described briefly with reference data. The fact that the new column, which is described in detail, employs complete condensation permits recovery of distillates of ether liquid or gas at will. Arrangement of the column head and accessories allows desired reflux conditions and the maintenance of constant operating adjustments. The possibility of overheating or overcooling of the temperature indicators is prevented, and progress of the fractionation is followed easily by true temperature measurement with thermometer or thermocouple. Manipulation of the column, with a glass tube spiral as exchanger, is described. Efficiency is demonstrated by separation of mixtures of propene-propane, isobutane-butane, and motor-fuel oil. In addition to the form of column for preparation purposes, an analytical arrangement also is described. Illustrated.

1825. ———. [Hydrocarbons Boiling Below 100° in Synthetic Gasoline From Carbon Monoxide and Hydrogen (Kogasin).] Brennstoff-Chem., vol. 22, 1941, pp. 135–139, 145–152; Chem. Abs., vol. 36, 1942, p. 5331.

Olefins were separated from paraffins by means of the $Hg(OAc)_2$ method. Tests showed that this method also can be used for ditertiary olefins; for example, C_2Me_4. The 2 hydrocarbon groups were further split up by fractional distillation. For this purpose a packed column (23 in. high, heated by oil circulation) and several glass spiral columns (80, 160, and 320 cm. high) were made. The applicability of the semimicrofractionating column with a rotating metal band of Lesesne and Lochte type (Chem. Abs., vol. 32, 1938, p. 7310) was extended by various additions. The paraffin mixture was separated into its individual components by 58 fractional distillations, most of which occupied several days. Besides the predominant n-paraffins, n-C_5H_{12}, -C_6H_{14}, and -C_7H_{16}, the following pure isoparaffins were isolated: $MePr^B$, β- and γ-methyl-pentane and –hexane, and the presence of $CHEt_3$ was proved. Multibranched paraffins were present only in traces, if at all. The olefin mixture was separated by 134 fractional distillations into the following: $\Delta\alpha$– and $\Delta\beta$–pentene, –hexene, and –heptene, as well as $CHPr\beta$. CH_2, ξ-methyl-$\Delta\alpha$, hexene, a mixture of γ- and ξ-methyl-$\Delta^{a'}$-pentene, and a mixture of γ- and ϵ-methyl-Δ^{a}-hexene. The olefins were identified by their physical properties and partly by hydrogenation reactions. The olefins consisted mainly of unbranched α- and β-olefins. Besides these, small quantities of α-olefins singly methylated outside the double linking were found. The presence of other types of olefins can be assumed but quantitatively they are negligible. Appreciable amounts of tertiary but no quaternary C were found in the products from Co catalysts.

1826. ———. [Polymerization of Monoolefins to Viscous Oils.] Brennstoff-Chem., vol. 23, 1942, pp. 67–73; Chem. Abs., vol. 36, 1942, p. 4701.

Properties of polymer lubricating oils, having the structure of the olefins charged to the polymerization process, were investigated. Most of the olefins used were obtained from the gasol and the light gasoline of the Kogasin process. The olefins with 5–7 C atoms, liquid at room temperature, were polymerized at 0° and 15°, respectively, under comparable conditions. Viscosities and yields of the resulting products vary greatly. It appears that these differences are due to the olefins belonging to different groups, of which the following four were noted: (1) Straight-chain α-olefins; (2) Branched α-olefins, the branch not starting on one of the double-bond C atoms; (3) Straight-chain β-olefins; (4) Branched β-olefins, with the branch starting on one of the double-bond C atoms. The reaction temperature is critical for the polymerization of the isobutene, while it is not critical when polymerizing olefins belonging to 1 of the groups 1–3.

1827. Koch, H., and Horn, O. [Comparative Investigation of Motor Behavior of a Synthetic Naphtha (Kogasin I) by Fischer-Tropsch and a Petroleum Naphtha.] Brennstoff-Chem., vol. 13, 1932, pp. 164–167; Ges. Abhandl. Kenntnis Kohle, vol. 11. 1934, pp. 530–536; Chem. Abs., vol. 26, 1932, p. 3657.

Various 10° fractions of the 2 naphthas have been examined and compared for density, unsaturated hydrocarbons, I number, C_6H_6 number and octane number. With increasing boiling point of the fractions. unsaturated hydrocarbons decrease from 46–23% in the synthetic product but increase from 16.5–29% with the petroleum fuel. Antiknock rating decreases from 85–41.5 octane no. with the synthetic, and from 77–54.5 with the petroleum fuel.

1828. Koch, H., and Ibing. G. [Composition of Hard Paraffins Produced in the Naphtha Synthesis of F. Fischer and H. Tropsch.] Brennstoff-Chem., vol. 16, 1935, pp. 141–148; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 402–419; Petrol. Refiner, vol. 22, 1943, pp. 279–286; Chem. Abs., vol. 29, 1935, p. 5642.

Separation of the high-molecular hydrocarbons by various methods has been studied, and the extraction and reduced pressure-distillation methods have been investigated. Extraction with ether, dichloroethylene, and $CHCl_3$ indicates possible separation into groups of similar molecular weight and properties. Repeated distillation at 10^{-5} mm. Hg did not greatly concentrate individual hydrocarbons. Molecular weights increased uniformly with melting point. n-Paraffins to as high as $C_{35}H_{72}$ are indicated; they melt at 117° and have a molecular weight of 2,000.

1829. ———. [Diesel Oil Obtained in the Benzine Synthesis of F. Fischer and H. Tropsch. Isolation and Chlorination of Symmetrical Paraffin Hydrocarbons.] Brennstoff-Chem., vol. 16, 1935, pp. 185–190; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 420–433; Chem. Abs., vol. 30, 1936, p. 1984.

Diesel oil, in part dewaxed Kogasin II, was subjected to vacuum distillation. Normal paraffins from decane to octane were isolated. The remaining 60–70% of the paraffins consisted of isoparaffins. The n-paraffins were chlorinated and fractionated by vacuum distillation. Bibliography is given.

1830. ———. [Constitution of Lubricants Prepared From Kogasin II.] Brennstoff-Chem., vol. 16, 1935, pp. 261–268; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 465–481; Chem. Abs., vol. 30, 1936, p. 1985.

Alkyl chlorides previously prepared were condensed in the presence of active Al or condensed with aromatic hydrocarbons in the presence of $AlCl_3$. Reaction products were separated by distillation and the composition of the fractions was determined. Viscosities and viscosity-temperature curves are given.

1831. Koch, H., and Küster, H. [Catalytic Reduction of Carbon Dioxide With Hydrogen.] Brennstoff-Chem., vol. 14, 1933, pp. 245–251; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 249–262; British Chem. Abs., 1933, B, p. 737; Chem. Abs., vol. 27, 1933, p. 5154.

Catalyst of Co and Ni for the synthesis of benzine is very effective at 150° in the production of CH_4. Traces of CO- and O_2-containing compounds were found in a few cases. With a large excess of CO_2, complete equilibrium is reached, which at 150°–400° is almost completely toward the CH_4 side. Adding steam at the start strongly retards the reaction by increasing the H_2 concentration. When blast-furnace gas treated with steam is used, a N_2-diluted CO_2-H_2 mixture is obtained, which, passed over CO, gives CH_4. CH_4 is obtained quantitatively from a similar CO-H_2-N_2 mixture passed over Ni. Passing CO and steam over Ni gives 3:1 CO_2 and CH_4. MeOH, a possible intermediate compound, is completely decomposed in the presence of CO_2 over Ni at >200°. S compounds poison the catalysts.

1832. Koch, H., and Richter, H. [Isomerism Equilibrium of Hexane.] Ber. deut. chem. Gesell., vol. 77, 1944, pp. 127–132; Chem. Abs., vol. 39, 1945, p. 903.

1833. ———. [Isomerization of Butene.] Oel u. Kohle, vol. 40, 1944, pp. 231–241; British Abs., 1948, B, II, p. 285; Chem. Abs., vol. 44, 1950, p. 5307.

When n-C_4H_8 is isomerized at 190° on a Fischer-Tropsch catalyst, a shifting of the ethylenic linking and cis-trans-conversion takes place, yielding an equilibrium mixture that accords with that calculated by Frost from free energies of the isomers. At higher temperature and pressure, slight cracking occurs and a red polymer is formed as a byproduct. Active C catalyzes the shift of the ethylenic linking at 325°, the main reaction being a redistribution of H_2, with formation of C_4H_{10} and higher unsaturated hydrocarbons. Al_2O_3 catalyzes this shift at 190°, but at 400° iso-C_4H_8 is formed accompanied by cracking, which gives C_3H_6 and polymerization leading to C_8H_{16} as main product. In presence of H_2 phosphates of Cd as catalyst formation of iso-C_4H_8 occurs at a lower temperature and is accompanied by polymerization; at a higher temperature polymerization is reduced, but the catalyst soon loses its activity. If in the Fischer-Tropsch synthesis, C_4H_8-isomers are added to the reactant gases, besides hydrogenation, shift of the ethylenic linking occurs, by which the composition of the residual C_4H_8 approaches the equilibrium for n-C_4H_8; C_2 hydrocarbons are not produced from C_2H_4 in this reaction.

1834. Koch, H., and Steinbrink, H. [Synthesis and Hydrogenation of Polyalkylated Benzenes.] Brennstoff-Chemie, vol. 19, 1938, pp. 277–285; Chem. Abs., vol. 33, 1939, p. 150.

Preparation of hydrocarbons with lubricating properties has been attempted in the preparation of alkylated benzenes of high molecular weight, similar to the Kogasin products, and their hydrogenation to the corresponding cyclohexane derivatives.

1835. ———. [Cracking of Paraffin Wax by Action of Aluminum Chloride Formed in Situ.] Brennstoff-Chem., vol. 20, 1939, pp. 147–152; Chem. Abs., vol. 34, 1940, p. 6053.

By treating a natural or a Kogasin paraffin wax with activated Al (5–10% of the wax)+HCl at 210°–260° (15–120 hr.), yields of 40–60% of gasoline and 10–15% of gasol were obtained. The gasoline contained no detectable quantities of C_6H_6 or toluene. It consisted principally of paraffin hydrocarbons but contained also some alkyl chlorides. Part of the latter tained also some alkyl chlorides. Part of the latter decomposed on distillation; olefins were formed.

1836. KOCH, H., AND TITZENTHALER, E. [Determination of the Degree of Branching in Synthetic and Natural Solid Paraffins With the Help of Hydrogenating Decomposition on a Cobalt Catalyst.] Brennstoff-Chem., vol. 31, 1950, pp. 212–221; Chem. Abs., vol. 44, 1950, p. 9335.

Various synthetic and natural solid paraffins were decomposed by hydrogenation on a Fischer-Tropsch Co catalyst within the temperature range 180°–230°. The liquid hydrocarbons obtained with the main product CH_4 were analyzed in the boiling range 30°–170° by close fractionation. Since by demethylation splitting, branching is preferably maintained in the same positions, quantitative conclusions can be drawn from the amount of isocompounds in the decomposition product as to the original isocontent of the initial paraffin. Taking a straight-chain paraffin, n–octadecane, for example, it can be shown that even with careful decomposition a limited amount (about 4%) of branched hydrocarbons formed through isomerization must be reckoned with. A synthetic gatch fraction obtained on a Co or Fe catalyst yielded about 30% of isoparaffin, while a synthetic hard paraffin gave an average proportion of branched compounds of 38%. A soft paraffin from the spindle-oil fraction of an Emsland crude oil yielded 8% and a hard paraffin separated from the machine oil fraction 24% of isocompounds. A Tief-Temperatur Hydrierung brown-coal paraffin showed about 11% of branched hydrocarbons. The hydrogenating decomposition also was accompanied to a limited extent by aromatization whereby the methylated aromatics appeared to a large extent as benzol. Tests on the splitting hydrogenation of paraffin on active Fe catalysts did not produce the desired results at the temperatures employed up to 350°. It was further discovered that Co catalysts temporarily lose their ability to split hydrocarbons by hydrogenation when small amounts of NH_3 are added to the H_2.

1836a. KOCH, H., AND VAN RAAY, H. [Individual Branched Hexenes and Their Isomerization Equilibria.] Brennstoff-Chem., vol. 32, 1951, pp. 161–174; Chem. Abs., vol. 45, 1951, p. 8238.

During the war, catalytic isomerization reactions were of importance in increasing the octane number of synthetic gasoline; such reactions are also of importance in preparing a variety of products from the alcohols obtained in the oxo synthesis by varying the position of the double bond. The reaction mechanisms of the isomerization of olefins and isomerization dehydration of alcohols are reviewed. A Co gasoline-synthesis catalyst permitted equilibrium to take place smoothly in an autoclave at 190° between 2, 3-dimethyl-1-butene and 2, 3- dimethyl-2-butene while the isomerization of the 2-methylpentenes did not progress under similar conditions.

1837. KOCH, H., PICHLER, H., AND KÖLBEL, H. [Fatty Acids Obtained in Small Amounts in the Benzine Synthesis of F. Fischer and H. Tropsch.] Brennstoff-Chem., vol. 16, 1935, pp. 382–387; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 433–443; Chem. Abs., vol. 30, 1936, p. 3970.

Formic, acetic, propionic, and butyric acids were identified in the 0.35% yield obtained with Co catalysts in the synthesis. These acids are found in the reaction liquor, of which 2/3 is acetic. No unsaturated acids were found. Acids dissolved in Kogasin were 0.06% of the latter, mostly of 5–10 C atoms and a small amount still higher.

KOCH, H. W. *See* abs. 1233.

1838. KOCH, W. [Electrolytic Separation of Carbides in Alloy and Carbon Steels.] Stahl u. Eisen, vol. 69, 1949, pp. 1–8; Chem. Abs., vol. 43, 1949, p. 5718.

It is possible to isolate carbides in ferritic-pearlitic steels without breaking them down. When performing the separation in heat-treated steels in the transition or martensite phase, the C remains in the residue. The investigation of these carbides is difficult because of the surface activity of these materials. Electron microscopy was used, and photographs are shown.

1839. KODAMA, S. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. I. Studies by the Heating-Curve Method of the Catalytic Activity of a Few Metals. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 8, 1929, pp. 277–283; abstract sec. 2, 1929, pp. 35–36; Jour. Soc. Chem. Ind. (Japan), vol. 32, suppl., 1929, pp. 4, 6, 23; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 12, 1930, pp. 193–204; Chem. Abs., vol. 23, 1929, p. 3844; vol. 24, 1930, p. 2663.

Ni, Co and Fe are reduced at various temperatures, and their catalytic activity in the reduction of CO by H_2 under atmospheric pressure is measured. The mixture of 1 mol. H_2+1 mol. CO is passed through 2 tubes, 1 with and 1 without catalyst and heated progressively to 400°. A differential thermocouple records the exothermic reaction. After the reaction, the Ni dissolved in the HCl without leaving any residue, while Co left a residue of C. The activity of Ni is thus independent of the temperature of reduction, while the opposite is true with Co. In the absence of H_2, both Ni and Co catalyze the decomposition of CO. Fe reduced at 350° and 450° shows an exothermic reaction around 300° which is caused principally by the oxidation of Fe. The Fe catalyst is then no longer active, and is found to be a mixture of FeO and C. Furthermore, the heating curve with CO alone is virtually identical with that of CO+H_2.

1840. ———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. II. Study by the Heating-Curve Method of the Influence of a Few Substances on the Catalytic Activity of Cobalt. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 8, 1929, pp. 284–287; abs. sec. 2, 1929, pp. 36–37; Jour. Soc. Chem. Ind. (Japan), vol. 32, suppl., 1929, pp. 4, 6, 23; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 12, 1930, pp. 205–210; Chem. Abs., vol. 23, 1929, p. 3844; vol. 24, 1930, p. 2663.

Influence of K_2CO_3, Cu, ThO_2, Al_2O_3 and MnO on the activity of a Co catalyst was studied by the method described above. The decomposition of CO with separation of C is not evident when ThO_2 or Cu is added to it. ThO_2 and Cu to a less degree increase the activity of Co toward the reduction of CO and the formation of hydrocarbons. Al_2O_3 and MnO are detrimental to the activity of Co.

1841. ———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. III. Preparation of Liquid Hydrocarbons With a Cobalt-Copper-Thoria Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 32, suppl., 1929, pp. 285–286; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 12, 1930, pp. 211–224; Chem. Age, vol. 27, 1929, p. 406; Chem. Abs., vol. 24, 1930, p. 2036.

Reaction begins at 100°; liquid products were observed. The best temperature is 252°; at higher temperature the greater part of the CO decomposed becomes CO_2 and CH_4 hydrocarbons, and there is little oil formation. The reaction temperature is lower than that given in the literature. At 248°, 84.4 l. of the gas mixture at a velocity of 5 l. per hr. gave 3.85 cm.³ H_2O, 0.45 cm.³ petroleum, and 0.4 cm.³ benzine.

1842. ———. Catalytic Reduction of Carbon Oxide Under Ordinary Pressure. IV. Influence of Beryllium Oxide, Magnesium Oxide, Zinc Oxide and Cadmium on the Cobalt-Copper Catalyzer. Jour. Soc. Chem. Ind. (Japan), vol. 33, suppl., 1930, p. 60; Sci. Papers Inst. Phys. Chem. Research (Tokyo),

vol. 13, 1930, pp. 93–105; British Chem. Abs., 1930, A, p. 551; Chem. Abs., vol. 24, 1930, p. 2979.

Study of the influence of BeO, MgO, ZnO and Cd on the Co–Cu catalyst for the synthesis of petroleum hydrocarbons from water gas at atmospheric pressure has shown that MgO is the best accelerator, being most active at 240° and giving the highest yields. BeO is most active at 260°; however, the yields are small. ZnO is the poorest accelerator, the reaction starting at 260°. Cd completely destroys the activity of Co.

1843. ———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. V. Influence of Titanium Oxide, Zirconium Oxide and Cerium Oxide. Jour. Soc. Chem. Ind. (Japan), vol. 33, suppl., 1930, pp. 202–203; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 14, 1930, pp. 13–25; Chem. Abs., vol. 24, 1930, p. 4376.

To determine the most effective catalyst for synthesizing petroleum from water gas the influence of TiO_2, CeO_2 and ZrO_2 was examined. The catalyst containing 3 parts Co, 1 part Cu, and the above oxides was reduced at 300° from the oxides derived from the nitrates. The gas mixture contained equal parts of CO and H_2 and was passed over 30 gm. of catalyst at 5 liter per hr. Catalysts containing TiO_2, ZrO_2 or CeO_2 give liquid products at 180°–200° and all show similar gas contractions. With TiO_2 gas contraction diminishes to 26.1% after 12 hr., then gradually to 40.7% after 39 hr., forming mainly gaseous hydrocarbons. ZrO_2 is the best, but not as good as MgO. CeO_2 is the poorest accelerator.

1844. ———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. VI. The Hydrocarbon-Forming Action of Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 33, suppl., 1930, pp. 399–400; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 14, 1930, pp. 169–183; Chem. Abs., vol. 25, 1931, pp. 496, 1039.

Fe catalysts for synthetic hydrocarbons are of greater commercial importance than those containing Co. No experimental details on Fe catalysts have yet appeared. Fe catalysts produce no H_2O; Co catalysts always, sometimes several times as much as hydrocarbon. The CO_2 content of the reaction gas is about 20% when using Fe catalysts; with Co 5–10%. The unconverted reaction gas with Fe catalyst contains more CO than H_2; with Co the opposite. Fe catalysts give a colored oil; Co seldom a yellow, never a colored benzine. Fe catalysts require higher temperature than Co. Catalysts containing mostly Fe withdraw O of the CO in the form of CO_2. Since CO is more decomposed than H_2, the H_2 content of the final gas is always greater than the CO content; with Co, vice versa. A catalyst containing Fe 1, Cu 1, Na_2CO_3 0.02, gives the best yield, 1.8 cm.³ kerosine and 1.4 cm.³ benzine from 157.0 l. of gas, which is lower than that from Co–Cu catalysts containing MgO or ZrO_2. Addition of MgO to the Fe catalyst injured it. Without addition of alkali an Fe–Cu catalyst forms only lower hydrocarbons.

1845. KODAMA, S. AND FUJIMURA, K. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. VII. Effect of Alkalies on Iron-Copper Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 34, suppl., 1931, pp. 14–16; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 29, 1936, pp. 272–279; Chem. Abs., vol. 25, 1931, p. 1952; vol. 30, 1936, p. 8570.

With a Cu–Fe catalyst prepared from the nitrates, 3.0 cm.³ of oil containing a small quantity of a substance like vaseline was obtained at 270° from 141 l. of water gas. Addition of 0.0005–0.05 mol. of Na_2CO_3 to the above catalyst increased its initial activity and favored formation of higher hydrocarbons. With catalysts containing alkalies there is a high gas contraction at first, the activity diminishing gradually. The catalyst may become coated with the higher hydrocarbon. No diminution of activity occurs with alkali-free catalysts. The best catalyst contains Fe 1 atom, Cu 1 atom, Na_2CO_3 0.005 mol.

1846. FUJIMURA, K. Catalytic Reduction of Carbon Monoxide at Ordinary Pressure. VIII. Iron-Copper Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 34, suppl., 1931, pp. 136–138; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 29, 1936, pp. 280–284; Chem. Abs., vol. 25, 1931, p. 4173.

Three catalysts in which the ratio of Fe to Cu was 5:1, 3:1 and 1:2 were studied in the formation of hydrocarbons from water gas at about 275° and atmospheric pressure. The 1st catalyst was most reactive, and the other 2 had approximately the same reactivity. About 3.3 cm.³ of liquid hydrocarbon was produced from 140 l. of gas with each catalyst.

1847. ———. Catalytic Reduction of Carbon Monoxide under Ordinary Pressure. IX. Additional Tests With a Co–Cu–MgO Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 34, suppl. 7, 1931, pp. 227–229; Chem. Abs., vol. 25, 1931, p. 5341.

Tests were made to determine the relation between catalyst activity and volume; a pumice support is used in 1 case and a light-sugar charcoal support in the other. With the first catalyst the gas contraction was about 40%, and 38.4–46.6 cm.³ of oil was produced from 68.7–75.3 l. of gas, solid paraffin appearing in 1 case. With the voluminous catalyst the gas contractions were 60 and 34.5%, and the oil yields 36.6 and 27.0 cm.³ from 75.1 and 68.7 l. of gas respectively.

1848. ———. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. X. Influence of Certain Materials on the Catalytic Action of Cobalt-Copper-Magnesium Oxide Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 34, suppl., 1931, pp. 384–386; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 17, Nos. 333–338, pp. 11–15, 16–21; Chem. Abs., vol. 26, 1932, p. 900.

Under the conditions of previous tests Co–Cu–Mg–Th, 8:1:2:0.4, or Co–Cu–Mg–U, 8:1:2:0.4, were most effective; the yield of liquid products was 81.5 cc. per m.³ in 1 case. Addition of W, Mo or Cr oxide was not as good as addition of Th or U. The above catalysts were less effective when supported on voluminous sugar charcoal.

1849. ———. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressures. XI. Jour. Soc. Chem. Ind. (Japan), vol. 35, suppl., 1932, pp. 179–182; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 189–197; Chem. Abs., vol. 26, 1932, p. 4444.

Catalyst of Co–Cu–Th–U, 8:1:0.15:0.15, mixed with equal quantities of starch and carried on kieselguhr proved most satisfactory. The physical condition of the catalysts is as important as the chemical composition.

1850. FUJIMURA, K. AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressures. XII. Jour. Soc. Chem. Ind. (Japan), vol. 35, suppl., 1932, pp. 415–416; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 198–201; Chem. Abs., vol. 27, 1933, p. 16.

Irradiation of catalysts with 50-kv. x-rays was tried but without success. With a Cu–Co–Th–U catalyst 1 : 8 : 0.2 : 0.1 there was obtained 145 cc. benzine/m.³ gas in 1 passage. Changing the proportions of Th and U has no effect.

1851. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XIII, XIV. Nickel Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 36, suppl., 1933, pp. 119–121; Sci. Papers

Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 242–247, 248–253; British Chem. Abs., 1933, B, p. 452; Chem. Abs., vol. 27, 1933, p. 3133.

Most effective temperatures were 190°–220°. A catalyst of Ni+18% ThO₂ gave 108 cc. liquid/m.³ of gas mixture. Mn can be substituted for Th. Small amounts of alkali carbonates were effective as promoters. A catalyst of Ni+18% Mn+15 cc. Rb₂CO₃ (N/1400) also gave 108 cc. liquid.

1852. ⸺⸺. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressures. XV, XVI. Nickel Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 36, suppl., 1933, pp. 413–416; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 254–258, 259–263; Chem. Abs. vol. 27, 1933, p. 4997.

Ni catalysts with additions of Mn, Cr, Mo, W, U₃S, ThO₂, Al₂O₃ and fuller's earth as well as Ni, Mn and Cu combinations were tested. Best results were obtained with ThO₂, Al₂O₃ and fuller's earth additions. A catalyst consisting of Ni and 15% Mn and 0.5% Cu gave good results also.

1853. ⸺⸺. Synthesis of Benzine From Carbon Monoxide and Hydrogen under Ordinary Pressure. XVII. The General Properties and Chemical Composition of the Reaction Products. Jour. Soc. Chem. Ind. (Japan), vol. 37, suppl., 1934, pp. 395–400; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 24, 1934, pp. 79–92; Brennstoff–Chem., vol. 15, 1934, p. 412; British Chem. Abs., 1934, B, p. 662; Chem. Abs., vol. 28, 1934, p. 4655.

Products of the reaction were gases, oils and an aqueous solution. Composition of the gases varied widely. With a Co catalyst there was a little CO₂ and some hydrocarbons together with unchanged CO and H₂ but with Ni catalysts the hydrocarbons varied 6–35%. 80% of the oils distilled below 200° and the normal paraffins from C₅ to C₁₁ were identified. The use of Ni catalysts gave over 90% saturated hydrocarbons while Co gave up to 57% olefins. No aromatic hydrocarbons or naphthenes could be detected. The higher the boiling point of a fraction the less olefin it contained. Investigation of the aqueous solution showed small amounts of aldehydes, alcohols, acids, and ketones.

1854. 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. Jour. Soc. Chem. Ind. (Japan), vol. 37, suppl., 1934, pp. 395–400; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 24, 1934, pp. 93–102; Brennstoff–Chem., vol. 15, 1934, p. 412; British Chem. Abs., 1934, B, p. 662; Chem. Abs., vol. 28, 1934, p. 4655.

Action of H₂S and CS₂ was studied. Small amounts of either increased the activity of a Ni–Mn–(15%) Al₂O₃ (3%) (1) catalyzer but larger amounts poisoned it. They had no preliminary activating effect on a Ni–Mn(15%)–ThO₂(3%) (2) catalyzer and this was more easily poisoned. From 16–28 mg. H₂S or approximately 50 mg. CS₂/gm. Ni were required to halve the activity of (2) and 54 mg. H₂S/gm. Ni was required for (1). The poisoning power of the CS₂ increased directly the amount of CS₂, but that of the H₂S increased directly with the logarithm of the amount of H₂S. When a large amount of (1) was used H₂S had no effect on it up to a certain point, after which it poisoned it in the usual way. It was shown that excess catalyst had no effect on the reaction and that the necessary and sufficient quantity of catalyst was 2 gm. Ni when the oven temperature was 200°, the gas flow was 4 l./hr. and the volume ratio CO : H₂ was approximately 1 : 2. Under these conditions there was produced 135 cc. benzine/m.³ of gases used and 3.5% of the Ni was in an active condition.

1855. FUJIMURA, K. AND TSUNEOKA, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen Under Ordinary Pressure. XIX. Composition of the Initial Gas Mixture (1). Jour. Soc. Chem. Ind. (Japan), vol. 37, suppl., 1934, pp. 395–400; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 24, 1934, pp. 103–112; Brennstoff–Chem., vol. 15, 1934, p. 412; British Chem. Abs., 1934, B, p. 662; Chem. Abs., vol. 28, 1934, p. 4655.

It was theoretically deduced and proved by experiment that a volume ratio of CO : H₂ of 1 : 2–1 : 2.1 was the best for benzine synthesis. An excess of CO had little effect but excess H₂ caused an excessive production of CH₄.

1856. ⸺⸺. Benzine Synthesis From Carbon Monoxide and Hydrogen Under Ordinary Pressure. XX. Composition of the Initial Gas Mixture (2). Jour. Soc. Chem. Ind. (Japan), vol. 37, suppl., 1934, pp. 704–711; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 25, 1934, pp. 127–136; British Chem. Abs., 1935, B, p. 132; Chem. Abs., vol. 29, 1935, p. 1230.

When a mixture (I) of 32.8% CO, 65% H₂ and 2.2% N₂ was passed at the rate of 4 l./hr. over a 27-cm. contact layer of catalyzer (Ni+15% Mn+3% ThO₂+ 125% kieselguhr) containing 2.5 gm. Ni at 200°, 117 cc. of liquid benzine per m.³ of pure CO+2H₂ was obtained. Under the same conditions (I) containing approximately 10% N₂ gave 115 cc., 10% CH₄ 120 cc., 10% CO₂ 111 cc., 20% N₂ 112 cc., 20% CH₄ 106 cc., 20% CO₂ 91 cc., 40% N₂ 95 cc., 40% CH₄ 85 cc. and 40% CO₂ 90 cc. Thus less than 20% of inert gas did not seriously affect the reaction but 40% cut the yield considerably. Also the more the mixture was diluted, the lighter and more volatile was the oil produced. After removing the S compound and CO₂ from a commercial gas it was passed over a 47-cm. layer of catalyzer containing 3.5 gm. Ni under the above conditions. This gas (30.2% CO, 54% H₂, 4.7% CH₄, 10.9% N₂), containing 81% usable CO+2H, gave 98 cc. benzine/m.³ of gas or 121 cc./m.³ of pure CO+2H. Under like conditions (I) gave 137 cc./m.³ of pure CO+2H.

1857. TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXI. Relations of the Gas Composition to the Working Temperature and to the Degree of Saturation of the Benzine Respectively. Jour. Soc. Chem. Ind. (Japan), vol. 37, suppl., 1933, pp. 711–716; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 25, 1934, pp. 137–143; British Chem. Abs., 1935, B, p. 132; Chem. Abs., vol. 29, 1935, p. 1231.

Ni–Mn–Al₂O₃ catalyst is used. With the ratio of CO : H₂ in the initial gas above 1 : 2.0–1 : 2.1 the yield of benzine and the reaction velocity can be increased by raising the temperature. No CH₄ is formed if the temperature is kept below 200°–210°. If the H₂ content of the initial gas is increased, the temperature must be lowered to suppress the CH₄-synthesis reaction. There is a linear relationship between the H₂ content of the outlet gas and the I number of the benzine. The higher the H₂ content, the greater the saturation of the benzine. The volatility of the benzine increases with higher working temperatures.

1858. ⸺⸺. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXII. Usefulness of a New Alloy Catalyzer. Jour. Soc. Chem. Ind. (Japan), vol. 37, suppl., 1933, pp. 738–744; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 25, 1934, pp. 144–151; British Chem. Abs., 1935, B, p. 132; Chem. Abs., vol. 29, 1935, p. 1231.

Porous catalyzer of good thermal condition is obtained by dissolving out the Si from a Ni–Co–Si (1:1:2) alloy. With this catalyst, a benzine yield of

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108 cc. per m.³ is obtained at 180° by a single pass of the theoretical gas mixture. Increasing the temperature decreases the degree of saturation of benzine. Increasing the amount of the catalyst increases the benzine yield and lowers the working temperature.

1859. TSUNEOKA, S., AND MURATA, Y. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIII. The Extraction and Leaching Treatment of Alloy Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 38, suppl., 1935, pp. 199–206; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 27, 1935, pp. 13–22; Chem. Abs., vol. 29, 1935, p. 4551.

Experiments were carried out on the methods of preparation of Ni–Co–Si (1:1:2) catalyst to improve the activity of alloy catalysts. The extraction of Si from the alloy is an essential operation and the most favorable procedure consists in boiling 24 hr. with the theoretical amount of NaOH. Any residual alkali in the extracted catalyst exerts a detrimental influence upon its activity, and as complete a removal of alkali as possible is indicated. The residual alkali increases the power of CH₄ formation of the catalyst. The experiments with the Ni–Co–Si catalyst did not show any relation between the gas contraction and the benzine yield. The activity of the benzine catalyst becomes greater as the most favorable reaction temperature is lowered. With 25 gm. of Ni–Co alloy catalyst a maximum benzine yield of 120 cc. per m.³ was obtained in a single-pass operation with an initial gas composition of 33.5% CO, 65.6% H₂ and 0.9% N₂. Increase in quantity of catalyst resulted in a less volatile and more saturated benzine.

1860. ⸺⸺. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIV. The Influence of the Particle Size and the Hydrogen Treatment or Oxidation Conditions of the Alloy Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 38, suppl., 1935, pp. 206–212; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 27, 1935, pp. 23–31; Chem. Abs., vol. 29, 1935, p. 4551.

Activity of the catalyst became less with a decrease in particle size. The H₂ pretreatment of the Ni–Co–Si alloy catalyst is unimportant, almost no increase in activity being obtained by H₂ pretreatment at 220°. A H₂ treatment at 350°–450° is detrimental and at 450° it results in complete inactivation of the catalyst. Oxidation of the catalyst before and after H₂ treatment is likewise considered unfavorable.

1861. ⸺⸺. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXV. General Properties and Constituents of the Benzine Prepared With an Alloy Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 38, suppl., 1935, pp. 212–217; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 27, 1935, pp. 32–38; Chem. Abs., vol. 29, 1935, p. 4551.

Catalyst used was of the composition Ni : Co : Si= 1:1:2. Double fractionation with a Widmer column gave distillates at 30°–40°, 60°–70°, 90°–100°, 120°–130° and 140°–150°. About 75 vol. % were found to be distillable at 220°. The contents of unsaturated hydrocarbons were determined by the observation of density, and I number; they are lower for a higher boiling point. The method of Garner gave 90.5% paraffins and 9.5% olefins. The product was water white, had good volatility, did not contain any S compounds and diolefins, refining was not necessary and it had a high heating value.

1862. ⸺⸺. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVI. Gas Contraction and Benzine Synthesis. Jour. Soc. Chem. Ind. (Japan), vol. 38, suppl., 1935, pp. 569–575; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 28, 1935, pp. 48–56; Chem. Abs., vol. 30, 1936, p. 270.

No relation appears to exist between the total gas contraction and yield of benzine.

1863. ⸺⸺. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVII. Cobalt-Alloy Catalysts. Jour. Soc. Chem. Ind. (Japan), vol 39, suppl., 1936, pp. 267–273; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 30, 1936, pp. 1–14; British Chem. Abs., 1936, B, p. 1028; Chem. Abs., vol. 30, 1936, p. 8570.

Activity of Ni–Co–Si, Ni–Co–Mn–Si and Co–Si alloys has been improved by melting the original alloy in a high-frequency furnace. With 10 gm. Ni–Co–Si (1:1:2) alloy catalyst a maximum benzine yield of 130 cc. per m.³ was obtained from 1 m.³ of initial gas (33.6% CO and 65.4% H₂). A small addition of Mn to Ni–Co–Si alloy catalyst appears harmful. Mn checks hydrogenation of the catalyst and accelerates polymerization. The activity of Co–Si catalyst increases with decrease in particle size. H₂ treatment of Co–Si catalyst is detrimental. The optimum temperature for Co–Si catalyst is 230°. The activity is lower than that of Ni–Co–Si alloy catalysts.

1864. ⸺⸺. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVIII. Nickel Alloy Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 39, suppl., 1936, pp. 273–278; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 30, 1936, pp. 15–29; British Chem. Abs., 1936, B, p. 1028; Chem. Abs., vol. 30, 1936, p. 8570.

Activity of Ni–Al catalyst increases with a decrease of particle size. A H₂ treatment at 350° increases the activity, but at 450° complete inactivation results. CH₄ formation is most favorable at 240°–250°. The activity of Ni–Si catalyst increases with the decrease of particle size. No H₂ treatment is necessary for this catalyst. Though the optimum temperature of Ni–Si catalyst is lower than Co–Si, it has a lower activity. The addition of Mn to Ni–Si catalyst influences the activity unfavorably. The activity of Ni–Fe–Al (1:1:2) catalyst increases with decrease in particle size. H₂ treatment is unnecessary for this catalyst.

1865. ⸺⸺. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIX. Influence of Bore and Length of the Reaction Tube. Jour. Soc. Chem. Ind. (Japan), vol. 39, suppl., 1936, pp. 294–298; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 3, 1936, pp. 30–39; British Chem. Abs., 1936, B, p. 1028; Chem. Abs., vol. 30, 1936, p. 8570.

With 10 gm. of Ni–Co catalyst a bore of 13 mm. is most favorable. The smaller the bore the greater is the formation of gaseous hydrocarbons. The volatility of the benzine formed is dependent upon the bore and length of the reaction tube. The best length of reaction tube for a bore of 13 mm. or less is approximately 30 cm. A 20-mm. reaction tube must be longer than 50 cm. With constant bore the decrease of reaction tube length promotes the formation of gaseous hydrocarbons. With decrease in tube length the most favorable reaction temperature decreases. The volatility of the benzine formed is increased.

1866. ⸺⸺. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXX. Influence of Catalyst Concentration. Jour. Soc. Chem. Ind. (Japan), vol. 39, suppl., 1936, pp. 325–329; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 30, 1936, pp. 40–51; British Chem. Abs., 1936, B, p. 1028; Chem. Abs., vol. 30, 1936, p. 8570.

If more than a certain amount of catalyst is used, constant velocity being assumed, the reaction reaches a condition of equilibrium independently of the amount of catalyst used. This limiting value depends on the quality of the catalyst and the conditions of the experiment. Polymerization, hydrogenation, heavy hy-

drocarbon formation and CO_2 formation are promoted by the use of too large a quantity of catalyst. When the most favorable amount of catalyst is used the formation of gaseous hydrocarbons is at a minimum.

1867. MURATA, Y., ISHIKAWA, S., AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXI. Influence of Current Velocity. Jour. Soc. Chem. Ind. (Japan), vol. 39, suppl., 1936, pp. 329-333; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 30, suppl., 1936, pp. 52-59; British Chem. Abs., 1936, B, p. 1028; Chem. Abs., vol. 30, 1936, p. 8570.

Most favorable velocity for a 13-mm. bore is 4 l. per hr., corresponding to a mass velocity of 500. Wide variations in velocity do not markedly affect the most favorable reaction temperature, but marked changes occur in the composition of the benzine, the formation of CO_2, C_nH_{2n+2} and heavy hydrocarbons.

1868. TSUNEOKA, S., AND MURATA, Y. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXII. Studies on the Material of the Reaction Furnace. Jour. Soc. Chem. Ind. (Japan), vol. 40, No. 11, suppl., 1937, pp. 438-441; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 33, 1937, pp. 305-312; Chem. Abs., vol. 32, 1938, p. 1426.

Probable effect of using Fe, Ni, Cu, Al and brass furnaces on the yield of benzine has been studied by mixing small pieces of these metals with the alloy catalyst, Ni-Co-Si (1 : 1 : 2), and carrying out the synthesis in the normal manner (see abs. 1859). The metals used did not effect the yield and exerted no catalytic effect. It is suggested that Fe furnaces can probably be used most practicably for large-scale production.

1869. MURATA, Y., AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIII. Relation of Free Space in the Reaction Tube and the Reaction Rate of the Initial Gas, and Also the Influence of Materials Mixed With the Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 40, No. 11, suppl., 1937, pp. 438-441; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 33, 1937, pp. 313-332; Chem. Abs., vol. 32, 1938, p. 1426.

With a horizontal contact tube the contact between the incoming gas and the catalyst becomes insufficient when the free space above the catalyst goes above a certain limiting value. With a catalyst layer length of 30 cm. and a gas flow of 4 l. per hr. this maximum value is 13 mm. For a given gas-volume velocity and catalyst layer length this value decreases as the diameter of the tube is increased. Natural silica and Fe are useful as packing materials. Active charcoal and silica gel are unsuitable. The I-number of the generated benzine decreases if the catalyst is mixed with other substances; that is, if the free space in the reaction tube is decreased. When the catalyst is to be used with other substances complete mixing is necessary.

1870. TSUNEOKA, S., AND KURODA, R. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIV. Analytical Studies of Alloy Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 40, No. 11, suppl., 1937, pp. 449-451, 451-454; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 33, 1937, pp. 333-338, 339-346; Chem. Abs., vol. 32, 1938, p. 1426.

Ni-Co-Si (1 : 1 : 2) alloy catalyst prepared in a high-frequency furnace gave Ni 23.9, Co 22.6 and Si 50.5%.

1871. ——. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXV.

Microscopic Study of Alloy Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 40, No. 11, suppl., 1937, pp. 449-451, 451-454. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 33, 1937, pp. 339-346; Chem. Abs., vol. 32, 1938, p. 1426.

Shows photomicrographs of the following alloy catalysts: Co-Si (1:1); Ni-Si (1:1); Ni-Co-Si (1:1:2); Ni-Co-Si (1:1:2) after treatment with enough NaOH solution theoretically to remove 20% Si; Ni-Co-Si (1:1:2) after treatment with 50% of the amount of NaOH necessary for complete removal of Si; Ni-Co-Mg (1:1:2) after complete removal of Mg with (NH₄)₂ CO_2.

1872. TSUNEOKA, S., AND MURATA, Y. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVI. Relation of the Activity of the Catalyst to the Synthesis Requirements at Too High a Temperature. Jour. Soc. Chem. Ind. (Japan), vol. 40, No. 12, suppl., 1937, pp. 478-484, Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1937, pp. 68-82; Chem. Abs., vol. 32, 1938, p. 2715.

Influence of raising the optimum temperature of 195° to 300° has been studied. In the range 240°-250° no synthesis of benzine takes place; CH_4 and some H_2CO_3 are formed. At 270° benzine is again formed, but in small quantity. If the reaction is carried on at a temperature above the optimum and then brought back again to the optimum the catalyst loses its characteristic activity, depending on the amount of treatment at the high temperature. When the reaction has been carried on at a temperature higher than the optimum, any benzine subsequently formed at the optimum temperature will have a higher I number proportionate to the increase in temperature used in the previous treatment.

1873. TSUNEOKA, S., AND NISHIO, A. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVII. Volume Velocity of the Gas. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 11-16; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1937, pp. 83-98; Chem. Abs., vol. 32, 1938, p. 3592.

For given amounts of catalyst and fixed layer lengths, the yield of benzine decreases if the velocity of the current of gas is increased. With a fixed-gas volume velocity and catalyst-layer length, the yield of benzine obtained during an increasing velocity of the current of gas after it once reaches a maximum decreases gradually. The amount of unsaturation has a tendency to rise with the larger values of gas-volume velocity. In a reaction tube of 20 mm. width, with a constant gas-volume velocity (500), the unsaturation increases as the velocity of the current of a gas becomes larger. If the volume velocity of the gas is not large, the rate of production of CO_2 tends to increase with the amount of catalyst.

1874. MURATA, Y., AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVIII. Relation Between Conditions of Synthesis and the Unsaturation of the Benzine Produced. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 16-22; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1937, pp. 99-115; Chem. Zentralb., 1938, II, p. 2874; Chem. Abs., vol. 32, 1938, p. 3592.

Following are the I nos. of the benzines produced with different catalysts: Fe-Cu-Na₂CO₃ 150, Ni-Mn-Th₂O 7.5, Ni-Mn-Al₂O₃ 11.8, Ni-Si (1:1) 18.0, Co-Cu-U₂O₃ 82.2, Co-Cu-U₂O-Mn 98.9, Co-Cu-Th-U 100.0, Co-Si 88.3, Ni-Co 20.0 and Ni-Fe 51.8. Silica added to the catalyst decreases the I number. The highest I number is obtained with a reaction tube 13 mm. in diameter. It is possible to increase the content of

unsaturated hydrocarbons by increasing the CO in the original gas. The I number increases as the gas volume velocity and also the velocity of the current of gas increases. The temperature at which the benzine is synthesized may increase or decrease the I number, depending on the catalyst used.

1875. TSUNEOKA, S., AND MURATA, Y. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIX. Properties of a Precipitated Nickel-Cobalt Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 52-57; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 280-294; Chem. Abs., vol. 32, 1938, p. 3945.

Precipitated Ni-Co catalyst (I), without the addition of an accelerator, is useless for the production of benzine. With ThO_2 (II), Al_2O_3 or Cr_2O_3 as accelerators the optimum temperature of reaction is comparable to that of U_3O_8 (III). (II) and (III) are excellent accelerators while Mn is not very effective. With (I) the optimum amount of Mn is 15-20%. The optimum reduction temperature of a Ni-Co-Mn catalyst is at 350°, while if (II) or (III) is added, the reduction is more successful at 400°. The most suitable mixing proportions of Co and Ni are 1:1.

1876. ——. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XL. Proportions of Nickel and Cobalt, and the Influence of the Addition of Copper to the Precipitated Nickel-Cobalt Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 57-59; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 295-300; Chem. Abs., vol. 32, 1938, p. 3945.

Optimum reduction temperature decreases from 400° to 300° if 10% Cu is added to Ni-Co, 1:1, catalyst. The activity of (I), however, is decreased.

1877. KATAYAMA, I., MURATA, Y., KOIDE, H., AND TSUNEOKA, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLI. Activation of Catalysts by Slow Oxidation With Atmospheric Oxygen. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 393-399; Sci Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 1181-1196; Chem. Abs., vol. 33, 1939, p. 1261.

Catalyst (I) used in the work was a mixture of (50% Ni+50% Co)+15% Mn+5% U_3O_8+3% ThO_2+125% kieselguhr (see abs. 1875). A study was made of the change in activity of (I) caused by slow oxidation with air and the possibility of its storage-in air as a result of exposing a sample, freshly reduced with H_2, with and without a subsequent exposure to CO_2, to the oxidizing action of varying amounts of air at room temperature. In the experiments an amount of (I) was taken such that it contained 1.5 gm. each of Ni and Co, and which had a volume of about 30 cc. The reaction tube was hard glass of about 20 mm. diameter. Freshly reduced (I) showed an increase in activity when directly oxidized with 1,700-2,600 vol. of air at a velocity of 50-80 l. per hr. and with a maximum increase in activity of 10% with 130 vol. at 4 l. per hr. The oxidation of (I), previously treated with CO_2, with 4,500 vol. of air at a velocity of 140 l. per hr. increased the activity, and with 3,300 vol. at 4 l. per hr. the increase was about 8%. A freshly reduced (I), which had been treated first with CO_2 and then partly oxidized with air, is much less susceptible to further oxidation than is a freshly reduced (I) which has been partially oxidized with air but without the CO_2 treatment. (I) which has been activated by slow oxidation with air and then used in a benzine synthesis cannot be further activated by a subsequent oxidation. Samples of (I) which have received a slow and weak oxidation with air are stable to further exposure to the air, whereas (I), when freshly prepared by reduction with H_2, is rapidly oxidized on direct

exposure to the air with evolution of much heat, even to redness.

1878. TSUNEOKA, S., AND FUNASAKA, W. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLII. Purification of the Gaseous Raw Material Used for Benzine Synthesis. 1. Removal of Organic Sulfur Compounds at Low Temperature. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 43-47; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 301-309; Chem. Abs., vol. 32, 1938, p. 3577.

Researches were undertaken to find a satisfactory method of S removal, with known or new materials, from a gas to be used further for the synthesis of benzine, its S content to be less than 0.2 gm. S per 100 m.³ City gas, with a total S content of 24.0 gm. S per 100 m.³ of which 22.6 gm. S is organic, was freed of CO_2 and H_2S and as such used over adsorbent materials, dry purificants and H_2S extraction materials at room temperature. As adsorbent materials were used active C, SiO₂ gel, Japanese acidic-earths and Adosol. Active C was found the most efficient but not active enough to produce a highly purified gas. As dry purificants Fe_2O_3 on a pumice support and Luxmasse were used, as H_2S scrubbing materials Thylox solution and $(C_2H_4)_2N$ to which Fe_2O_3 was added were used. 80% S removal was obtained with the dry purificants. Thylox failed to extract the organic S, while with $(C_2H_4)_2N$, 67.7% S removal was obtained; it was further improved by addition of Fe_2O_3.

1879. ——. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLIII. Purification of the Gaseous Raw Material Used for Benzine Synthesis. 2. Removal of Organic Sulfur Compounds at High Temperature. Jour. Soc. Chem. Ind. (Japan), vol. 41, suppl., 1938, pp. 47-51; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 310-320; Chem. Abs., vol. 32, 1938, p. 3577.

Same city gas was used for S removal at high temperature by passing the gas through heated pipes without and in the presence of catalysts. Fe, Cu and V2A-steel pipes were used. At 500°, Fe pipe gave the best results but desulfuration is only 77%. Ag catalysts (1% Ag by wt.), CuO-CrO₄Pb, Ni, Fe-Cu, Ag catalysts (10% metal) and active C were used in an effort to eliminate the organic S by transforming it into H_2S by contact. With CuO-CrO₄ Pb, Ni, Fe-Cu catalysts (10% metal), at temperatures 450°, 350°, 300°, 330 cm.³ per hr. per cm.³ contact (see abs. 1026) in each case, the organic S content was reduced to less than 0.2 gm. S per 100 m.³ of gas. The amount of organic S changed into H_2S was very small, the major part of it being fixed on the catalyst. A preliminary extraction of H_2S from the gas is necessary, otherwise the amounts of total S, remaining in gas, are 0.66, 3.12, 0.82 gm. per 100 m.³ respectively. With Fe_2O_3 on a pumice support (30% Fe_2O_3) and Luxmasse, at 350° and 330 m.³ per hr. per cm.³ contact, the organic S was completely removed from the gas. No preliminary extraction of H_2S is necessary and the S is economically removed to less than 0.2 gm. S per 100 m.³ (organic S less than 0.07 gm. per 100 m.³, total S less than 0.07 gm. per 100 m.³ or 99.7% S removed). The Luxmasse used by the authors was a by-product obtained in the manufacture of Al ("red mud"), often used in city-gas plants for H_2S removal, which in muddy form contained 38.2% of H_2O. The material was dried for 12 hr. at 105° and then crushed to 3-5 mm. granules.

1880. 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. Jour. Soc. Chem. Ind. (Japan), vol.

42, suppl., 1939, pp. 9, 12; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1938, pp. 32–38; British Chem. Abs., 1939, B, p. 688; Chem. Abs., vol. 33, 1939, p. 3559.

Use of various addition agents to Luxmasse for the removal of organic S from a gas containing 30.1 gm. S per 100 m.³ of which 28.4 gm. S is organic was investigated. The addition of 1 wt. % of ThO₂, UO₂ or NaOH to Luxmasse should have little effect. The addition of 10% NaOH, Ba(OH)₂, ThO₂, Cr₂O₃, Al₂O₃ or K₂CrO₄ improved the efficiency and the life of the Luxmasse. For the greatest efficiency Luxmasse containing 10% NaOH and 10% ThO₂ was used. At 400°, this mixture removed 98.9% of the S. The addition of Na₂CO₃ was not very promising.

1881. ————. 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. Jour. Soc. Chem. Ind. (Japan), vol. 42, suppl., 1939, pp. 9, 12; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1938, pp. 39–46; British Chem. Abs., 1939, B, p. 688; Chem. Abs., vol. 33, 1939, p. 3559.

With the same gas many synthetic masses were used for the removal of organic S. A mixture of Fe₂O₃–Al₂O₃–brimstone and NaOH (Fe 10%, Fe₂O₃:Al₂O₃= 1:1 and 1% NaOH) at 450° and a gas rate of 330 l. per hr. reduced the S to 0.19 gm. per 100 m.³ A 7:3 mixture of Luxmasse and diatomaceous earth with 30% NaOH at 350° and a gas rate of 330 l. per hr. reduced the S to 0.07 gm. per 100 m.³ A mixture of Fe₂O₃–bentonite–NaOH containing 10% Fe and 10% NaOH at 400° and a gas rate of 790 l. per hr. reduced the S to 0.16 gm. per 100 m.³ With the Fe₂O₃–Al₂O₃– diatomaceous earth–NaOH mass, the presence of CO₂ was harmful. Diatomaceous earth is the best carrier and materially increases the life of the purification mass.

1882. TSUNEOKA, S., MURATA, Y., AND MAKINO, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVI. Preparation of New Iron Catalysts and Their Superior Properties. Jour. Soc. Chem. Ind. (Japan), vol. 42, suppl., 1939, pp. 107–112. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 330–336; Chem. Abs., vol. 33, 1939, p. 4761.

Two new catalysts of Fe base were prepared: (I) is composed of Fe 4, Cu 1, kieselguhr 5 and K₂CO₃ 0.09. (II) consists of Fe 4, Cu 1, Mn 0.08, kieselguhr 5 and K₂CO₃ 0.09. Solutions of Fe(NO₃)₃, Cu(NO₃)₂ and accelerator were mixed with unpurified kieselguhr and precipitated with an equivalent solution of alkali carbonate in the cold. The precipitate was filtered on a porcelain filter, washed with warm H₂O, impregnated with a small amount of alkali, dried in air at 100° and pulverized. With (I) a gasoline yield of 88 cc. per m.³ and I number 141.0 is possible. (II) produced a yield of 88 cc. per m.³ of gasoline having an I number of 132. The Fe catalyst is cheaper than Co and Ni catalysts, and with it water gas can be used directly as a starting material. A reaction temperature of 250° is required as compared with 200° for Co and Ni catalysts, and its durability is slightly lower.

1883. ————. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVII. Composition of Starting Gases With New Iron Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 42, suppl., 1939, pp. 107–112; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 337–347; Chem. Abs., vol. 33, 1939, p. 4761.

Tabular results are given for experiments with CO and H₂ in the following ratios: 4:1, 3:1, 2:1, 1:1 and 1:2. With a catalyst consisting of Fe+25% Cu (by

weight of Fe)+125% kieselguhr+3% K₂CO₃, highest gasoline yields resulted from an initial gas mixture ratio of CO:H₂=1:1–1:2. An initial gas ratio of 1:2 was found most conducive to high yields with a catalyst comprising: Fe+5%Ni+25% Cu+125% kieselguhr+3% K₂CO₃. The larger the CO content of the gas the greater the degree of unsaturation of the gasoline. Excess H₂ produces no deleterious effects on the synthesis. The gasoline resulting from the synthesis employing the new Fe catalysts is colorless and clear. Water hinders the progress of the reaction. Volatility and degree of unsaturation increase with higher reaction temperatures. H₂ reduction increases the activity of the catalysts.

1884. MURATA, Y., MAKINO, S., AND TSUNEOKA, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVIII. Influence of Addition of Copper and Alkali on New Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 42, suppl., 1939, pp. 107–112; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 348–355; Chem. Abs., vol. 33, 1939, p. 4761.

Experiments carried out with a catalyst containing Fe+125% kieselguhr +3% K₂CO₃ (% based on weight of Fe) to which various amounts of Cu were added show that best gasoline yields were obtained by addition of Cu in amounts of 20–40% of the weight of Fe. The addition of 2–3% of alkali carbonate (K₂CO₃) to catalysts of composition Fe+25% Cu+125% kieselguhr, and Fe+5% Ni+25% Cu+125% kieselguhr increases the yield for CO:H₂ ratios both of 1:1 and 1:2. In general, however, the larger the CO content of the gases the smaller should be the addition of alkali. Degree of unsaturation increases with increasing amounts of alkali.

1885. ————. Synthesis of Benzine from Carbon Monoxide and Hydrogen at Ordinary Pressure. XLIX. Influence of Various Metals, Metal Oxides and Precipitants on Fe–Cu–Kieselguhr Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 42, suppl., 1939, pp. 107–112; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 356–364; Chem. Abs., vol. 33, 1939, p. 4762.

Addition of U₃O₈, ThO₂, Al₂O₃ and Cr₂O₃ to Fe–Cu–kieselguhr catalysts brings about very poor gasoline yields, especially with the last 2 oxides. The addition of 2% Mn or MgO to a catalyst consisting of Fe+25% Cu+125% kieselguhr+2% K₂CO₃ produces a yield of 88 cc. per m.³ The presence of Ni accelerates the reaction provided the CO:H₂ is 1:2. Co is less harmful than Ni. H₂O formation is noticed if the catalyst contains more than 2.5% Ni. Gasolines produced with Ni catalysts also have a low I number. Addition of ThO₂, U₃O₈, etc., to an Fe catalyst containing 10% Ni proved ineffectual. Na₂CO₃ is the most suitable precipitant for producing the catalyst. Replacing the carbonate with caustic soda proved damaging.

1886. FUNASAKA, W. Benzine Synthesis From Carbon Monoxide and Hydrogen. L. Removal of Organic Sulfur Compounds From Water Gas. Jour. Soc. Chem. Ind. (Japan), vol. 43, suppl., 1940, pp. 200–203; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 37, 1940, pp. 323–330; Chem. Zentralb., 1941, I, p. 849; Chem. Abs., vol. 34, 1940, p. 6796.

In contrast to the previously tested city gas, water gas containing 11.7 gm. total S per 100 m.³ and 11.0 gm. organic S per 100 m.³, from which the H₂S had been removed by treatment with Thylox solution (1.5% Na₂CO₃; 0.7% As₂O₃), could not be freed sufficiently from S compounds to be suitable for use in the benzine synthesis, which requires less than 0.2% S per 100 m.³, by treatment at 250° with Luxmasse, Luxmasse+10% NaOH, Luxmasse+Na₂CO₃ (2:1), ignited Fe₂O₃–Al₂O₃– diatomaceous earth–NaOH (1:1:2 with 10% NaOH),

ignited Fe₂O₃–Al₂O₃–pumice–NaOH (1:1:2 with 10% NaOH, Luxmasse–diatomaceous earth–NaOH (7:3 with 30% NaOH) or ignited Fe₂O₃–bentonite (containing 10% Fe), with a total of 150 l. of gas, a gas velocity of 30 l. per hr., a space velocity of 400, and a 25 cm. layer of treating agent. Total S contents of the treated gas samples (gm. S per 100 m.³) were 1.72, 1.88, 1.90, 1.30, 9.30, 3.68, and 4.05, respectively. 10% of an equimolecular mixture of Fe and Cu on pumice and of Ni on pumice lowered the S content of the water gas to 0.43 and 0.85 gm. S per 100 m.³, respectively. Temperatures above 250° resulted in C formation from the CO of the water gas; thus at 350°, although the S content of the gas was reduced to less than 0.07 gm. per 100 m.³, the Luxmasse+10% NaOH contained much C from energetic decomposition of CO.

1887. ————. Benzine Synthesis From Carbon Monoxide and Hydrogen. LI. Highly Active Sulfur–Fixation Agent Which Purifies Water Gas to the Highest Degree at Comparatively Low Temperatures. Such as 200°–250°. Jour. Soc. Chem. Ind. (Japan), vol. 43, suppl., 1940, pp. 203–206; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 37, 1940, pp. 331–337; Chem. Zentralb., 1941, I, p. 849; Chem. Abs., vol. 34, 1940, p. 6796.

At 250° under the conditions mentioned previously, water gas containing 18 gm. total S per 100 m.³ and 14.6 gm. organic S per 100 m.³ showed the following total S content after treatment with the agent mentioned: Luxmasse, 1.72; Luxmasse+10% Ni hydroxide (precipitated by addition of NaOH solution to hot NiSO₄ solution). 0.35 (0.30 with 900 l. gas; 0.97 at 200°, 250 space velocity. 40 cm. layer of treating agent and 30 l. per hr. gas stream velocity); Luxmasse+20% Ni hydroxide. 0.34; Luxmasse+10% Ni hydroxide+10% NaOH. 0.50 (0.44 with 900 l. gas); Luxmasse+10% Cu hydroxide (prepared similarly to Ni hydroxide). 0.30 (0.42 at 200° with 150 l. gas; 0.75 at 200° with 900 l. gas); Luxmasse+10% Cu hydroxide+10% NaOH. 0.18 (0.77 for 900 l. gas; 0.54 and 1.05 at 200° for 150 and 900 l. gas, with 250 space velocity and 40 cm. layer of agent; 0.26 and 0.14 at 200° for 150 and 100 space velocity and 60 and 45 cm. layer of agent, respectively); Luxmasse +20% Cu hydroxide+10% NaOH. 0.16; Luxmasse+ 10% commercial CuO+10% NaOH. 1.24; Luxmasse+ 20% commercial CuO+10% NaAH. 0.58; Luxmasse+ 30% commercial CuO+10% NaOH. 0.21; and Luxmasse +10%Cu hydroxide+10%NaOH (2 successive treats), 0.21. The efficiency of each fixation agent containing Cu rapidly decreased with use.

1888. MURATA, Y., AND MAKINO, S. Benzine Synthesis From Carbon Monoxide and Hydrogen. LII. Influence of the Initial Materials, Carriers and Filling Agents Upon the Iron Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 43, suppl., 1940, pp. 210–215; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 37, 1940, pp. 338–349; Chem. Zentralb., 1941, I, p. 849; Brennstoff-Chem., vol. 24, 1943, p. 9; Chem. Abs., vol. 34, 1940, p. 6796.

In the benzine synthesis at 257° from gas containing approximately equal proportions of H₂ and CO, with catalyst having the composition Fe+25% Cu+125% kieselguhr+2% K₂CO₃, best results were obtained with the catalyst precipitated from the nitrate solution (by K₂CO₃ solution), inferior results with that from chloride solution, and no reaction at all where precipitation was made from sulfate solution. The best carrier for the catalyst Fe+25% Cu+2% Mn+2% KOH (Na₂CO₃ precipitation agent) was 125 wt. % of kieselguhr (based on Fe present), Mn being somewhat inferior and A–carbon giving no yield of benzine. When used with Fe+25% Cu+125% kieselguhr+2% KOH (K₂CO₃ precipitation agent) and pumice, soda-lime, Mn, CaO and BaO were all good filling agents.

With Fe+25% Cu+125% kieselguhr (K₂CO₃ precipitation agent) the following catalyst addition agents (2% based on Fe present) are arranged in the order of decreasing effect on the catalyst; Rb₂CO₃ (additional 2% Mn)>KOH >KNO₃ >Rb₂CO₃ >KMnO₄ >K₂CO₃ >Na₂CO₃ >KCl. the benzine yield being much lower when KCl was present than when either of the other catalyst addition agents was present. Optimum quantities of K₂CO₃, KOH, Rb₂CO₃ and KMnO₄ for use as catalyst addition agents (with respect to quantity of Fe present) were 2%, 2%, 2–3% and 2–5% respectively. The use of Fe+25% Cu+2% Mn+125% kieselguhr +2% Rb₂CO₃ catalyst at 257° resulted in a benzine yield of 90 cc. per m.³

1889. MAKINO, S., KOIDE, H., AND MURATA, Y. Benzine Synthesis From Carbon Monoxide and Hydrogen. LIII. Influence of Aluminum Oxide, Silver, and Other Addition Agents Upon the Iron Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 43, suppl., 1940, pp. 235–241; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 37, 1940, pp. 350–365; Chem. Zentralb., 1940, I, p. 2842; Brennstoff-Chem., vol. 24, 1943, p. 9; Chem. Abs., vol. 34, 1940. p. 6797.

When precipitated with Fe+25% Cu+2% Mn+125% kieselguhr+2% KOH catalyst or when Al₂O₃ was added before precipitation, Al₂O₃ decreased the yield of benzine at 250° from gas containing approximately equal amounts of CO and H₂. When 1–3% Al₂O₃ was added (based on Fe present) after precipitation of the catalyst, the benzine yield was increased (94 cm.³ per m.³ with 3% Al₂O₃). Addition of the following Al compounds (2–5% with respect to Fe present) to the above catalyst resulted in decreasing yields of benzine in the order shown: AlPO₄>Al acetate >Al silicate>Al (OH)₃ >Al₂(SO₄)₃. The yield of benzine was 0 when Al₂(SO₄)₃ of AlCl₃ was added to the catalyst. Acid–clay (containing approximately 15% Al₂O₃) added to the above catalyst in quantities up to 25% (based on Fe present) increased the benzine yield. but when the acid clay was substituted for a portion of the kieselguhr of the catalyst, inferior yields were obtained. Coprecipitation of Ag (3–30%, based on Fe content) with the above catalyst or addition of 3–10% Ag₂O to the catalyst resulted in unchanged or diminished yields of benzine. Substitution of the Cu of the catalyst by 10, 20 or 30% Ag (based on Fe present) resulted in very inferior yields of benzine and the formation of some paraffin wax. Precipitation of 2–5% (based on Fe present) of Ba, Ca, Cd, Bi, Pb, Sn or W with the above catalyst resulted in inferior yields of benzine, Bi, Pb and W giving especially low benzine yields.

1890. MURATA, Y., AND YAMADA, T. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. LIV. Influence of Carbon Dioxide in the Initial Gas Upon the Iron Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 44, suppl., 1941, pp. 33–38. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 38, 1940, pp. 118–131; Chem. Zentralb., 1941, I, p. 2203; Brennstoff-Chem., vol. 24, 1943, p. 9; Chem. Abs., vol. 35, 1941, p. 2297.

When a gas mixture containing varying quantities of CO₂ and approximately equal volumes of CO and H₂ was passed over a catalyst consisting of Fe+25% Cu +125% kieselguhr+2% KOH at 253° at a rate of 3.8–4.3 l. per hr., the yield of liquid product and the I number of the liquid product decreased rapidly with increase in the CO₂ content of the gas charged, the effect being much greater than a simple diluent effect. Experiments with catalysts composed of Fe+25% Cu+2% Mn+125% kieselguhr and 0–5% KOH at 254° showed that the yield of liquid product and the C:H₂ ratio of the gas resulting from the reaction increased with increase in alkali content of the catalyst; with a catalyst composed of Fe+25% Cu+2% Mn+125% kieselguhr+2% KOH at 254° the yield of liquid prod-

uct increased with a decrease of gas velocity to 2.6 l. per hr., when the gas charge contained approximately 20% CO_2. When the catalyst was pretreated with CO_2, the yield of liquid products from CO and H_2 decreased with the increase in length of the CO_2 pretreatment; the CO_2 apparently decreased the activating effect of alkali on the catalyst. At 253° there was very little reaction between CO_2 and H_2 in the presence of Fe+25% Cu+125% kieselguhr+2% KOH.

1891. ———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. LV. Influence of Nitrogen, Methane, Oxygen, and Ammonia in the Initial Gas Upon the Iron Catalyst. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 38, 1941, pp. 218–229; Brennstoff-Chem., vol. 24, 1943, p. 10; Chem. Abs., vol. 35, 1941, p. 5284.

When a mixture of approximate molecular proportions of CO and H_2 is diluted with N_2 and passed at 253° over catalyst having the composition Fe+25% Cu+125% kieselguhr+2% KOH and at a gas velocity of 3.4–4.1 l. per hr., the yield of liquid product decreases, with respect to CO and H_2 with increasing amount of N_2 in the initial gas mixture, and the I number of the liquid product increases. This effect of N_2 in the initial gas mixture is observed when the catalyst has high activity. When the initial gas is diluted with CH_4, the effect is similar but much less (very little effect when the initial gas contains less than 10% CH_4) than when either N_2 or CO_2 is used as a diluent. Oxygen strongly decreases the yield of liquid products (initial gas containing 12.6% O_2 decreased the yield 83.3%, based on the CO and H_2 present) and the I number of the liquid produce increases moderately with increasing O_2 content of the initial gas. When the initial gas mixture contained 5% and 15% respectively of NH_3, the yields of liquid product were decreased 19.5% and 93%, based on the CO and H_2 present.

1892. KODAMA, S., TARAMA, K., OSHIMA, T., AND FUJITA, K. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Atmospheric Pressure. Analysis of the Synthetic Oil by Precision Distillation. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, suppl. binding, pp. 270–272; Chem. Abs., vol. 44, 1950, p. 7509.

Analytical distillations over a Podbielniak column were carried out on the gasoline fraction (obtained by sorption on activated C), naphtha fraction, hydrogenated naphtha fraction and the C_6–H_8 portion of the latter, all derived from the product obtained at 245°–250° from a synthesis over approximately equal parts of CO and H_2 with an Fe catalyst containing Cu 25, Mn 2, kieselguhr 125, H_3BO_3 20, and K_2CO_3 3%. The same type of distillation was applied to the naphtha fraction and the hydrogenated naphtha fraction from the oil obtained at 210°–212° from 1 part CO and 2 of H_2 with a Co catalyst containing Cu 10, Th 5, U 2.5, kieselguhr 125%. The C_5 and C_6 fractions each contained the following % by volume of n– and iso-hydrocarbons, respectively : Gasoline from Fe catalyst 61.8, 38.2; 56.3, 41.3; naphtha fraction from Fe catalyst 59.4, 40.6; 56.3, 43.7; hydrogenated oil from Fe catalyst 61.1, 38.9; 53.8, 46.2; naphtha fraction from Co catalyst 63.0, 37.0; the same, hydrogenated 72.0, 28.0; 57.0, 43.0.

1893. MURATA, Y., TATSUKI, Y., YAMADA, H., AND SAWADA, Y. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LVII. Effect of Some Added Substances on Iron–Copper Catalysts. Jour. Soc. Chem. Ind (Japan), vol. 45, 1942, pp. 557–560, suppl., pp. 229–232; Chem. Abs., vol. 43, 1949, p. 2399.

Effect of organic acids and other compounds on Fe–Cu catalysts was studied. With Fe catalysts the results were as follows: (1) $K_2C_2O_4$, HCO_2K, KOH, K_2CO_3, and KNO_3 accelerated the action, and the op-

timum amount of each is about 1.5% as K. (2) Organic acids were injurious. (3) $Cr(NO_2)_2$, CrF_3, $Cr_2(CO_3)_3$, and $Cr(OAc)_3$ were injurious to the catalyst but Cr_2O_3 was not. (4) $Zn(NO_2)_2$, ZnO, $Zn_3(PO_4)_2$, $Zn(OAc)_2$, and Zn stearate were injurious, but $Zn(OH)_2$ was not. Because of the action of H_3BO_3 Zn borate had an accelerating action.

1894. MURATA, Y., SAWADA, Y. AND TAKEZAKI, Y. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LVIII. Mutual Influence of Boric Acid and Alkali in Promoting Activities of Iron–Copper Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 670–675; Chem. Abs., vol. 43, 1949, p. 2399.

Mutual influence of diatomaceous earth, H_3BO_3, and alkali on Fe–Cu catalysts was investigated. The activating action of H_3BO_3 is very weak for Fe catalysts with no alkali; it increases with the addition of alkali. H_3BO_3 prevents the formation of high molecular hydrocarbons, such as solid paraffins, and promotes the formation of saturated hydrocarbons. With increases in the amount of H_3BO_3 added the durability of the catalyst increases.

1895. MURATA, Y., AND YASUDA, M. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LIX. Activation of Iron–Copper Catalysts by Boron. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 675–677; Chem. Abs., vol. 43, 1949, p. 2400.

Various B compounds were added to Fe catalysts, and their influence was studied. Mn and Mg borates have the same action as H_3BO_3. The addition of B compounds is effective even by mechanical mixing, while alkali has no effect by the same treatment.

1896. MURATA, Y., YASHIRO, R., AND TASHIRO, E. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LX. Effect of Copper on Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1117–1121; Chem. Abs., vol. 43, 1949, p. 2400.

Cu has excellent accelerating action on the activity of Fe catalyst, and the optimum amount of Cu is different for catalysts of different compositions. When H_3BO_3 and alkali are added, the optimum amount of Cu is about 10%. Cu has no effect on the durability of Fe catalysts. The composition of the feed gas has no effect on the optimum amount of Cu. The amount of Cu has no effect on the optimum reaction temperature. The effect of alkali on the Fe catalyst is not affected by the amount of Cu present.

1897. MURATA, Y., YOSHIOKA, Y., OJI, G., AND SAITO, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXI. Reaction Temperature and Durability of Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1271–1286; Chem. Abs., vol. 43, 1949, p. 2400.

Durability of Fe catalysts on the composition Fe: Cu : Mn : kieselguhr : H_3BO_3 : K_2CO_3=100 : 25 : 2 : 125 : x : y, where x=0 or 20 and y=1, 2, 3 or 4 in powdered form, and x=20 and y=4 in tablet form, used in the Fischer synthesis with a gas mixture (CO : H_2=1:1) at 200°–270° was studied. The optimum value of y is 2 to 4 when x=0 or 20, respectively, regardless of the reaction temperature, and an increase in y diminishes the durability of the catalyst. The promoting effect of H_3BO_3 is not noticeable below 220°, and the optimum reaction temperature is not affected by the addition of H_3BO_3. On the whole an Fe catalyst is active at 230°–260°, and its durability can be greatly increased by choosing a lower reaction temperature. The optimum reaction temperature can be lowered more when the catalyst is used in the form of tablets than when used in powdered form, probably because of the rise in temperature of the catalyst layer. The lower the activity of the catalyst, the higher is its durability.

1898. ———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXII. Durability of Iron Catalysts and the Composition of Gas Used in the Synthesis. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1271–1286; Chem. Abs., vol. 43, 1949, p. 2400.

Fischer synthesis was carried out with catalysts similar in composition to those used in preceding experiments with mixtures of composition CO : H_2=1 : 2, 1 : 3 and 1 : 5. With increase in H_2 content the most suitable reaction temperature was lowered, and the durability of Fe catalyst was remarkably increased. Thus with a mixture of CO : H_2=1 : 2 or 1 : 3 the same catalyst can be used continuously for about 1 month at a suitably fixed reaction temperature. With a mixture of CO : H_2=1 : 2, the highest yield of oil was 102 cc./m.³ of gas used, which decreased in proportion to dilution of the gas with more H_2. In these cases a small amount of H_2O was produced along with the oil. The property of H_3BO_3 in promoting the catalytic activity decreased with increases in H_2 content. With gas of composition CO : H_2=1 : 2 the addition of H_3BO_3 increased the durability of the catalyst, but with gas containing more H_2 it showed no effect.

1899. ———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXIII. Iron Catalysts and the Composition of Gas Used in the Synthesis. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1271–1286; Chem. Abs., vol. 43, 1949, p. 2400.

Fischer synthesis was carried out with a gas mixture of composition CO : H_2=2 : 1 with an Fe catalyst of high activity containing H_3BO_3. The yield of oil was much smaller with gas of composition CO : H_2= 2 : 1 than with composition 1 : 1. The durability of the catalyst was also reduced. Further, the relations between the composition of gas mixture after the reaction, the ratio of consumption of CO to H_2, properties of the oil obtained, the composition of the feed gas, etc., were summarized.

1900. MURATA, Y., NAKAGAWA, M., TASHIRO, E., AND UMEMURA, T. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXIV. Methods of Preparing Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 52–68; Chem. Abs., vol. 43, 1949, p. 2400.

In the preparation of Fe catalysts the effect of the precipitating method and temperature, the method of washing the precipitate, the concentration at the time of precipitation, the quality and preliminary treatment of kieselguhr, the purity of reagents, the amount of alkali used in precipitation, the method of adding alkali as promoter, etc., on the activity of the catalyst was studied. The catalyst containing Fe 100, Cu 25, kieselguhr 125, and K_2CO_3 2 parts by weight was used with a gas mixture of CO : H_2=1 : 1 at 253°. The results show: (a) It is desirable in the precipitation that alkali should be added as quickly as possible with sufficient agitation and the time of adding kieselguhr has no marked effect, (b) the temperature at the time of precipitation has little influence, (c) washing the precipitate requires special care but less than with Co or Ni catalysts, (d) the concentration of the reagents has no marked influence, but it is desirable that the alkali solution be concentrated and the solutions of metallic salts be rather dilute, (e) the quality of the kieselguhr has a marked effect, and kieselguhr previously treated with acid produces a catalyst of inferior quality, (f) Fe and Na_2CO_3 need not be especially pure (g) 5–15% excess of the precipitating reagent should be used, (h) it is necessary that the alkaline promoter be uniformly spread over the surface of the catalyst.

1901. ———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXV. Reduction by Hydrogen and Heat Treatment of Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 52–68; Chem. Abs., vol. 43, 1949, p. 2401.

Effect on the activity of Fe catalysts of various compositions by reducing with H_2, reoxidizing with air, and heating (without reduction) in a current of air was studied. Fe catalysts lose their activity when reduced with H_2 according to the temperature and time; thus they totally lose their catalytic power when reduced in H_2 4–8 hr. at 450°, while those reduced at 250° for 4–10 hr. regain their activity in the course of 1–2 days of normal operation. The activity of the catalysts reduced with H_2 is not recovered by oxidation with air at 250°–450°. Fe catalysts slightly increase their activity when heated in an air current at 100°–400°, but when the temperature is above 400°, the activity is gradually reduced with the elevation of temperature until at 600° it is completely lost.

1902. ———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXVI. Reduction of Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 52–68; Chem. Abs., vol. 43, 1949, p. 2401.

Effect on the activity of the catalyst of reducing with various gas mixtures was studied in detail. The activity of the catalyst is increased when it is reduced by H_2 to which a small amount of CO is added. The effect of adding CO is nearly linear up to CO : H_2=1 : 2 and diminishes gradually when more CO is added. When the ratio of CO : H_2 exceeds that of the gas mixture used in the synthesis, the activity of catalyst is greatly reduced. When the catalyst is reduced with a gas mixture rich in H_2 and used in the synthesis with gas of composition CO : H_2=1 : 2, the durability of the catalyst is greatly increased. Dilution of H_2 with N_2 shows no advantage, and the reduction with mixtures of CO and N_2 is unfavorable.

1903. FUNASAKA, W., AND TOJO, T. Synthesis of Gasoline From Carbon Monoxide and Hydrogen. LXVII. Desulfurizing Ability of Various Metal Hydroxides. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 402–403; Chem. Abs., vol. 43, 1949, p. 2401.

To remove the organic S in water gas the mixtures of hydroxides of Fe, Ni, Co, Cu, Mn, or Cd with kieselguhr were very effective. To remove the organic S in water gas by transforming into H_2S, mixtures of $Al(OH)_3$, $Mg(OH)_2$, and kieselguhr effective.

1904. TARAMA, K., TATSUKI, Y., KASAI, K., AND TAKEGAMI, Y. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXVIII. Analysis of the Synthetic Oil by Fractional Distillation. (2). Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 533–535; Chem. Abs., vol. 43, 1949, p. 2401.

Fractional distillation of oil synthesized with Fe catalyst confirmed that the synthetic oil consists mainly of aliphatic hydrocarbons and does not contain the aromatic hydrocarbons.

1905. KODAMA, S., MURATA, Y., AND HARA, I. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXI. Activity and Deactivation of Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 50, 1947, pp. 119–120; Chem. Abs., vol. 44, 1950, p. 9135.

Gasoline was synthesized 29 hr. from CO and H_2 in a molecular ratio of 1 : 1 at 250° with (A) Fe+12.8% Cu or (B) Fe+25% Cu+152% kieselguhr. The addition of K_2CO_3 and H_3BO_3 increased the activity of these catalysts. The optimum amount of K_2CO_3 was 1% for (A) and 2% for (B).

1906. MURATA, Y. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXII. Composition of Gases and Flow Velocity. Jour. Soc. Chem.

Ind. (Japan), 1947, vol. 50, pp. 120–121; Chem. Abs. vol. 44, 1950, p. 9135.

In the synthesis of gasoline with Fe catalysts, carbides and free C were formed by the activation of CO. The use of a gas mixture with a high H_2 content prevented this and the velocity of gas flow could be increased.

1906a. MURATA, Y., MATSUMOTO, E., AND HOSHINO, S. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXIII. Action of Carbon Monoxide on Iron Catalysts. Jour. Chem. Soc. Japan, ind. chem. sec., vol. 53, 1950, pp. 298–300; Chem. Abs., vol. 46, 1952, p. 11,632.

Influence of the pretreatment with pure CO on the activity of Fe catalysts was studied. The longer the time of pretreatment the smaller the gas velocity and the higher the temperature. The effect of pretreatment can be enhanced by adding alcohol.

1906b. MURATA, Y. AND HARA, I. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXIV. Influence of Water Vapor on Iron Catalysts. Jour. Chem. Soc. Japan, Ind. Chem. sec., vol. 53, 1950, pp. 338–340; Chem. Abs., vol. 46, 1952, p. 11,632.

Influence of water vapor on the activity of Fe catalysts has been studied under various conditions. Moisture contained in reacting component gases, however small the quantity may be, spoils the activity of Fe catalysts in almost all cases.

KODAMA, S. *See* abs. 2196, 3315, 3316, 3317.

KODAMA, S. AND FUJIMURA, K. Catalytic Reduction of Carbon Monoxide Under Ordinary Pressure. VII. Effect of Alkalies on Iron-Copper Catalysts. *See* abs. 1845.

1907. KODAMA, S., AND TAHARA, H. X-ray Investigation of Iron Catalyst Used in the Synthesis of Gasoline. I. Preliminary Report. Jour. Soc. Chem. Ind., Japan, vol. 45, 1942, pp. 1260–1262; Chem. Abs., vol. 42, 1948, p. 6082.

Freshly prepared catalyst for the hydrogenation of CO, consisting of Fe 100, Cu 25, Mn 2, kieselguhr 125, and K_2CO_3 2 parts was amorphous. Heating at 700° for 6 hours destroyed the catalytic power and produced α Fe_2O_3. Reduction in H_2 at 450° also destroyed the catalytic power and produced α Fe. After use in the synthesis of gasoline at 255° for 2 hours the catalyst had a spinel structure with lattice constant 8.4 A. As the catalytic activity diminished from too long use or from use at too high temperature, the X-ray lines corresponding to spinel disappeared, and new lines appeared corresponding to a face-centered lattice of constant 3.6 A. These results cannot yet be interpreted.

KODAMA, S., HONGO, M., AND TAHARA, H. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. XII. Catalyst Carrier. *See* abs. 1914.

KODAMA, S., MATSUMURA, S., AND ANDO, T. Physicochemical Investigations on Gasoline Synthesis. V. Velocity of Adsorption of Hydrogen by a Catalyst of Cobalt and Infusorial Earth. *See* abs. 2198.

———. Physicochemical Investigations on Gasoline Synthesis. VI. Velocity of Adsorption of Hydrogen by Cobalt-Thoria–Infusorial Earth Catalyst. *See* abs. 2199.

KODAMA, S., MATSUMURA, S., AND TARAMA, K. Physicochemical Investigations on Coal Synthesis. IV. Velocity of Adsorbing Hydrogen by Cobalt. *See* abs. 2197.

KODAMA, S., MURATA, Y., AND HARA, I. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXI. Activity and Deactivation of Iron Catalysts. *See* abs. 1905.

1908. KODAMA, S., TSUNEOKA, S., AND FUJITA, T. Fischer Process—Japan. Jour. Fuel Soc. Japan, vol. 18, 1939, p. a7.

Two synthetic-gasoline plants of the Fischer process are being hastily constructed by the Mitsui Mining Co. at Miike and by the Manchurian Synthetic Fuel Co. at Chinchou. Both plants are of a similar capacity—30,000 tons of synthetic gasoline per yr.—and it is reported that they are nearly completed. Recently the Hokkaidō Artificial Petroleum Co. was established in cooperation with the Imperial Fuel Industry Co., with a capital of 70 million yen. The plant to be constructed by this concern will have a production of 140,000 tons of synthetic oil per yr. and will be erected by the end of 1940. As a semi-industrial test of the synthesis under pressure, continuous investigations are being carried out by the Imperial Fuel Research Institute on 3 types of reaction chambers made of 4 Fe tubes 25 mm. inside diameter and 500 mm. long, 2 tubes 35 mm. inside diameter and 510 mm. long, and 1 tube 55 mm. inside diameter and 520 mm. long were constructed and tested. The reaction chamber was heated by circulating outside the chamber machine oil of high flash point, heated to the desired temperature. The catalyst used was Co–Cu–Th–U–kieselguhr, 100 : 12.5 : 2.5 : 1.25 : 125, prepared by the precipitation method and formed in tablets. The gas velocity was 100 l. per hr. in all cases. Where the inside diameter of the reaction tube was 25 mm. and 35 mm., the yield of gasoline was 98 cc. per m.³ and 78 cc. per m.³, as compared with 110 cc. per m.³ and 101 cc. per m.³ in the small-scale experiments, but it decreased rapidly to 40 cc. per m.³ in the case of the 55-mm. tube. It was concluded that the use of such a large-diameter tube is difficult. Based on the results of the investigation, the capacity of the reaction chamber was enlarged so as to be able to treat 10 m.³ of raw gas per hr. A mixture of water gas and electrolytic H_2 was used, the average organic S content of which was reduced to 1.05 gm. S per 100 m.³ with a Luxmasse–NaOH–Cu(OH)₂ (100 : 10 : 10) at about 200° C. The test was continued for about 10 days. The average gasoline yield was 81–85 cm.³ per m.³ (100 cm.³ per m.³ pure base), compared with 120 cm.³ per m.³ in the small-scale experiment.

KODAMA, S., TAHARA, H., HONGO, M., AND FUJITA, H. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. XI. Alkalines Used in the Preparation of the Iron Catalyst and Chlorine as a Poison. *See* abs. 1913.

1909. KODAMA, S., TAHARA, H., IMAI, O., AND YAMADA, T. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Moderately High Pressure. V. Effect of the Increase of Reaction Pressure. Jour. Soc. Chem. Ind. (Japan), vol. 50, 1947, p. 121; Chem. Abs., vol. 44, 1950, p. 9135.

In gasoline synthesis at moderately high pressure with Fe catalysts the maximum yield of oil was obtained at 15 kg. per cm.³ With an increase of pressure the amount of K_2CO_3 added must be increased.

1910. KODAMA, S., TAHARA, H., TAKIGUCHI, K., TOSHIMA, S., AND IHARA, K. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Moderately High Pressure. VI. Promoter Action of Various Oxides. Jour. Soc. Chem. Ind. (Japan), vol. 50, 1947, pp. 121–122; Chem. Abs., vol. 44, 1950, p. 9135.

Various promoters were tried. The optimum conditions were found with an Fe catalyst with Cu 25, Mg 5, kieselguhr 125 and K_2CO_3 6%. At a pressure of 10 kg./cm.³ and 210° with a molecular ratio of CO : H_2 of 1 : 1 yield of oil was 111 gm. per m.³

1911. KODAMA, S., TAHARA, H., NAKBAYASHI, T., AND HONGO, M. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. IX. Influence of the Composition of the Raw Gas on the

Reaction. Jour. Chem. Soc. Japan, ind. chem., sec., vol. 51, 1948, pp. 23–24; Chem. Abs., vol. 44, 1950, p. 9135.

With H_2 : CO ratios in the raw gas of 1.1, 2.0, or 2.7 oil yields are 61.57, or 50 gm. per m.³, respectively, with H_2 : CO consumption ratios of 0.7, 1.0, or 1.4 respectively with a catalyst of Fe+Cu 25+kieselguhr 125+K_2CO_3% at 10 kg. per cm.³ pressure and 210°. Under similar conditions the addition of 16% CO_2 (CO : H_2=1 : 1) decreases the oil yield, but 5% CO_2 does not. A determination of N(CO : H_2=1 : 2) up to 33.4% does not affect the yield for practical purposes.

1912. ———. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. X. Dependence of the Oil Yields on the Gas Flow. Jour. Chem. Soc. Japan, ind. chem. sec., vol. 51, 1948, p. 24; Chem. Abs., vol. 44, 1950, p. 9135.

With catalyst containing Fe+Cu 25+kieselguhr 125+K_2CO_3 6% at 10 kg. per cm.³ an increase in the flow rate from the standard value, 4 liter (N. T. P.) per hr., decreases the yield per unit volume and increases the yield per unit time at 210° and 230°, while a decrease of the flow rate decreases the yield per unit volume only slightly at 190° and 210°.

1913. KODAMA, S., TAHARA, H., HONGO, M., AND FUJITA, H. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. XI. Alkalies Used in the Preparation of the Iron Catalyst and Chlorine as a Poison. Jour. Chem. Soc. Japan, ind. chem. sec., vol. 51, 1948, pp. 24–25; Chem. Abs., vol. 44, 1950, p. 9135.

To conduct the reaction with a catalyst containing Fe+Cu 25+kieselguhr 125% at 10 kg. per cm.³ and 210° with a gas ratio CO : H_2=1 : 1 Na_2CO_3 is the best precipitating agent and addition of 6% K_2CO_3 to the catalyst is necessary. Cl in large amounts lowers the yield.

1914. KODAMA, S., HONGO, M., AND TAHARA, H. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. XII. Catalyst Carrier. Jour. Chem. Soc. Japan, ind. chem. sec., vol. 51, 1948, pp. 25–26. Chem. Abs., vol. 44, 1950, p. 9136.

In the synthesis at 210° and 10 kg. per cm.³ several carriers (125% of the Fe) are substituted for kieselguhr with different amounts of alkaline salt. The oil yields decrease in the order: kaolin>active earth>acid earth>bentonite, their maximum yields being 70, 50, 40 and 25 gm. per m.³ respectively, with 4, 6, 8 and 6% K_2CO_3, respectively. As much as 90 gm. per m.³ oil can be obtained by the most favorable composition. (Fe+Cu 25+kaolin 150+K_2CO_3 4%).

KODAMA, S., TAHARA, H., NAKBAYASHI, T., AND HONGO, M. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. IX. Influence of the Composition of the Raw Gas on the Reaction. *See* abs. 1911.

KODAMA, S., TAHARA, H., NAKBAYASHI, T., AND HONGO, M. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Elevated Pressures. X. Dependence of the Oil Yields on the Gas Flow. *See* abs. 1912.

1915. KODAMA, S., TARAMA, K., OSHIMA, T., AND FUJITA, K. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. I. Effect of Temperature With the Iron Catalyst. II. Effect of Rate of Flow of the Starting Gases With the Iron Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 44, suppl. binding, 1941, pp. 272–274, 274–275; Chem. Abs., vol. 44, 1950, p. 7507.

In order to synthesize predominantly C_4 hydrocarbons, a synthesis gas composed of equal parts of CO and H_2 was passed at temperatures varying from 242°–299° over an Fe catalyst containing Cu, 25; Mn, 2;

kieselguhr, 125; H_3BO_3, 20; K_2CO_3, 3%. Increase in temperature resulted in a decrease in CH_4 formation and a decrease in reaction velocity. The maximum yield of gasoline was reached at 250°, while the yield of C_4 hydrocarbons increased up to 270° and remained virtually constant above this temperature. Operation at 251°–253° with varying space velocities indicated that a space velocity of 180–200 represents the optimum for C_4 hydrocarbon production.

1916. KODAMA, S., TARAMA, K., MISHIMA, A., FUJITA, K., AND YASUDA, M. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. III. Influence of Copper, Manganese, Potassium Carbonate and Boric Acid on Iron Catalysts. IV. Influence of the Temperature of the Synthesis on Various Promoters in the Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 69–77; Chem. Abs., vol. 43, 1949, p. 2398.

K_2CO_3 greatly increased the mean molecular weight of the product, as did Cu to a lesser degree. The effect of adding H_3BO_3 and Mn was the reverse. However, the effect of these substances on the production of gasol (mixture of C_2H_6, C_3H_8 and C_4H_{10}) was not very marked, so that it was not possible to improve the production of gasol by the addition of these substances alone. On the contrary, the elevation of the temperatures of the synthesis had a remarkable effect in increasing the yield of gasol. Of the various catalysts used 100 Fe+125 kieselguhr gave the best results, yielding a product containing 78% gasol, although this catalyst had less power of causing CO and H_2 to react.

1917. KODAMA, S., TARAMA, K., MISHIMA, A., FUJITA, K., AND YASUDA, M. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide, and Hydrogen. V. Influence of Potassium Carbonate on Iron Catalyst. VI. Influence of Boric Acid on the Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 404–408; Chem. Abs., vol. 43, 1949, p. 2398.

Addition of K_2CO_3 increased the mean molecular weight of the hydrocarbons produced and decreased the formation of CH_4, while the addition of H_3BO_3 decreased the mean molecular weight.

1918. KODAMA, S., TARAMA, K., TAKAZAWA, T., FUJITA, K., TEJIMA, T., ITO, S., AND YOKOMAKU, Y. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. VII. Effect of Temperature on Synthesis With Cobalt Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2398.

Hydrocarbons were prepared from a 1 : 2 mixture of CO and H_2 by means of Co, 100; Cu, 12.5, ThO_2, 2.5; U_3O_8, 1.25; and diatomaceous earth 125 parts, a reaction temperature of 180°–290°, and a period of operation of 24 hr. Temperature elevation increased the yield of the lower hydrocarbons but did not increase the relative yield of CH_4, as was the case with the Fe catalysts. Usually with a Co catalyst a small elevation of temperature caused a remarkable increase in the yield of CH_4, but, from the results of these experiments, it was observed otherwise, although an increase in the relative yield of the gaseous hydrocarbons (CH_4, gasol) was noticeable. In short, it may be impossible to produce the gasol without the other components by elevating the temperature. In these experiments, the maximum yield of gasol was 18.9 l. per m.³ at 270°. In comparing Co and Fe catalysts, the difference is explained by evaporation of hydrocarbons from the surface of the catalyst and a decrease in adsorbed H atoms.

1919. ———. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. VIII. Effect of Composition of the Synthesis Gas on Iron

Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2398.

Catalysts of Fe, 100; Cu, 25; diatomaceous earth, 125, and K_2CO_3, 2 parts was used at 270° over a period of 6 hr. For the gasol synthesis the optimum $CO : H_2$ ratio is 50–60 : 50–40. For the least CH_4 production the ratio is 1 : 1. For maximum gasol production with least CH_4 the ratio is 1 : 1.5. In view of the life of catalyst the optimum ratio is 1 : 1.5.

1920. ――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. IX. Effect of Addition of Diatomaceous Earth on Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2398.

Catalysts of Fe 100+Cu 25 parts was used with CO and H_2 (1 : 1) at 270° over a period of 16 hr. The addition of diatomaceous earth improves the life of the catalyst; 125% diatomaceous earth is most suitable for gasol synthesis.

1921. ――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. X. Effect of Various Carriers on the Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949. p. 2398.

Catalysts of Fe 100, Cu 25, and K_2CO_3 2 parts was used with CO and H_2 (1 : 1.5). With active C, Murata reported that hardly any oil .was produced but the authors found an increase in the volatile fractions. With white clay the gasol yield is very small, but its composition is unusual; it is high in C, and C_2 hydrocarbons, and the degree of unsaturation is high, 70–85%. Japanese acid clay increases the yield of gaseous hydrocarbons, 125% giving maximum gasol, 27.4 l. per m.³

1922. ――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XI. Comparative Study of the Synthesis Under Normal Pressure and Other Pressures. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2399.

With a catalyst of Fe 100 and diatomaceous earth 125 parts, and CO and H_2 (1 : 1) at 270°–275° for a period of 2–4 hr., pressure increases the life of the catalyst and improves the yield of gasol, and especially the yield of oil.

1923. ――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XII. Effect of Pressure. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2399.

On use of a catalyst of Fe+25% Cu on 125% diatomaceous earth at 5–20 kg. per cm.², the yield of gasol and the rate of reaction show maximum values at 15 kg. per cm.² With the same catalyst+2% K_2CO_3 on 125% white clay at 5–40 kg. per cm.,² there was no change in the yield of oil. The gasol yield and rate of reaction were maximum at 15 kg. per cm.² No satisfactory explanation of the effect of pressure was made. The optimum pressure range was approximately 15–20 kg. per cm.² with a gasol yield of 30 l. per m.³

1924. ――――. Synthesis of Gaseous · Hydrocarbons From Carbon Monoxide and Hydrogen. XIII. Effect of Temperature at Constant Pressure. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2399.

Elevation of temperature increases the yield of lower hydrocarbons and therefore increases the yield of gasol, but increased yields of CH_4 also occur because of the increase in the reactivity of H_2. Thus an increase in gasol by the elevation of temperature without an increase in CH_4 cannot be expected. The optimum temperature range for gasol synthesis is 270°– 320°.

1925. ――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XIV. Effect of Various Carriers and Promoters. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2399.

Effect of white clay and active C as carriers for Fe+25% Cu+2% K_2CO_3 was studied. White clay increased the yield of hydrocarbons and decreased the reactivity of H_2. Active C increased the reactivity. The effect of K_2CO_3 on the following catalysts were studied : Fe+25% Cu+250% white clay, Fe+25% Cu +125% active C, and Fe+25% Cu+125% Japanese acid clay. K_2CO_3 increased the yield of higher hydrocarbons, decreased the reactivity of H_2, and increased the unsaturated content of the gasol.

1926. ――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XV. Summary of the Studies on the Synthesis Under Pressure. Jour. Soc. Chem. Ind. (Japan), vol. 48, 1945, pp. 3–8; Chem. Abs., vol. 43, 1949, p. 2399.

With Fe catalysts pressure increases the life of catalyst, and increases the total rate of reaction; the yield of gasol approaches 30 l. per m.³ Increase in the gasol yield is not attainable by greater elevation of temperature. The optimum temperature is 270°– 320°. The effect of pressure is comparatively complex. Raising the pressure increases the tendency to form higher hydrocarbons as well as lower hydrocarbons, especially CH_4 and C_2H_6, because of an increase in the reactivity of H_2. This fact is interpreted to be a peculiarity in the mechanism of the synthesis under pressure. Therefore, gasol synthesis in which a high degree of unsaturation is desired should be carried out with a catalyst containing white clay as the carrier or by adding K_2CO_3 to a catalyst containing acid clay or active clay to promote the adsorption of CO. By raising the temperature it is impossible to increase the yield of gasol without also raising the yield of CH_4, as is the case at ordinary pressure.

KODAMA, S., TARAMA, K.; OSHIMA, T., AND FUJITA, K. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Atmospheric Pressure. LVI. Analysis of the Synthetic Oil by Precision Distillation. See abs. 1892.

KODAMA, S., MATSUMURA, S., TARAMA, K., ANDO, T., AND YOSHIMORI, K. Physicochemical Research on Gasoline Synthesis. VII. Velocity of Adsorption of Hydrogen by Iron. See abs. 2200.

KODAMA, S., MATSUMURA, S., TARAMA, K., ANDO, T., AND YOSHIMORI, K. Physicochemical Research on Gasoline Synthesis. VIII. Velocity of Adsorption of Hydrogen by Iron on Infusorial Earth. See abs. 2201.

KODAMA, S., MATSUMURA, S., TARAMA, K., ANDO, T., AND YOSHIMORI, K. Physicochemical Research on Gasoline Synthesis. IX. Velocity of Adsorption of Hydrogen by a Composite Iron Catalyst. See abs. 2202.

KODAMA, S., MATSUMURA, S., TARAMA, K., ANDO, T., AND YOSHIMORI, K. Physicochemical Research on Gasoline Synthesis. X. Adsorption of Carbon Monoxide on Cobalt, Cobalt–Kieselguhr and Cobalt– Kieselguhr–Thoria Catalysts. See abs. 2203.

KODAMA, S., MATSUMURA, S., TARAMA, K., ANDO, T., AND YOSHIMORI, K. Physicochemical Research on Gasoline Synthesis. XII. Adsorption of Carbon Monoxide on Iron, Iron–Kieselguhr, Iron–Kieselgush–Copper–Manganese Catalysts. See abs. 2204.

KODAMA, S., TAHARA, H., TAKIGUCHI, K., TOSHIMA, S., AND IHARA, K. Gasoline Synthesis From Carbon Monoxide and Hydrogen at Moderately High Pressure. VI. Promoter Action of Various Oxides. See abs. 1910.

KODAMA, S., TARAMA, K., MISHIMA, A., FUJITA, K., AND YASUDA, M. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. III. Influence of Copper, Manganese, Potassium Carbonate and Boric Acid on Iron Catalsts. IV. Influence of the Temperature of the Synthesis on Various Promoters in the Catarlst. See abs. 1916.

KODAMA, S., TARAMA, K., MISHIMA, A., FUJITA, K., AND YASUDA, M. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. V. Influence of Potassium Carbonate on Iron Catalyst. VI. Influence of Boric Acid on the Iron Catalysts. See abs. 1917.

KODAMA, S., MATSUMURA. S., YOSHIMORI. K., NISHIBAYASHI, Y., KADOTA, N., AND IWAMURA, E. Physicochemical Studies on Gasoline Synthesis. XIII. XV. Influence of Potassium Carbonate and Boric Acid on the Activated Adsorption of Hydrogen and Carbon Monoxide on Iron Catalysts. See abs. 2205.

1927. KODAMA, S., TAHARA, H., FUKUSHIMA, I., IAWO, M., KOMAZAWA, S., AND KIMURA, K. Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen under Medium Pressure. II. Characteristics of Hydrocarbon Synthesis under Medium Pressures With an Iron Catalyst. Durability of the Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1263–1271; Chem. Abs., vol. 43, 1949, p. 2397.

Petroleum synthesis was carried out at 230°–260° under a pressure of 10 kg./cm.² with an equimolecular mixture of CO and H_2; 40 cc. of Fe catalyst of composition Fe : Cu : Mn : kieselguhr : H_2BO_3 : K_2CO_3=100 : 25 : 2 : 125 : 20 : 7 and a gas velocity of 6 m.³ at standard conditions/hr. were used continuously for 180 days to determine the durability of the catalyst. Catalyst durability under such conditions was excellent, and the rate of oil production of about 90 gm./m.³ could be maintained for 6 months by merely raising the temperature slightly. As the durability of the catalyst is very great even at higher reaction temperatures, Fe catalysts presumably have greater durability than Co catalysts under high pressure. Other characteristics of the medium-pressure process are the production of water with consequent diminution of CO_2 content in the waste gas and an increased need of solid paraffins in comparison with the synthesis carried out under atmospheric pressure. The production of CH_4 did not increase even when the activity of catalyst was increased by raising the temperature.

1928. ――――. Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen Under Medium Pressure. III. Effect of Adding Alkali and Changes in the Reaction Temperature on the Activity of Fe–Cu–Mn–H_2BO_3 Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1263–1271. Chem. Abs., vol. 43, 1949, p. 2397.

Catalysts with 7–20 parts K_2CO_3 and other components, as given above, were compared in medium-pressure petroleum synthesis to determine the optimum composition. The catalysts containing 7–10 parts K_2CO_3 gave the best yield of oil. The rate of consumption of CO compared to H_2, the amount of solid paraffin produced, and the degree of unsaturation of oil produced all increased with the increase in the amount of K_2CO_3 added. By trial, the best reaction temperature was found to be 230°–250°.

1929. ――――. Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen Under Medium Pressure. IV. Effect of Changing Alkali, Boric Acid, and Kieselguhr Contents on the Activity of Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 1263–1271; Chem. Abs., vol. 43, 1949, pp. 2397– 2398.

To determine the best composition of Fe catalysts to be used in medium-pressure petroleum synthesis, the effect of varying amounts of K_2CO_3, H_3BO_3, Cu and kieselguhr was studied. The addition of H_3BO_3 lowers the activity of Fe catalyst. The optimum amount of alkali is 4–5 parts when no H_3BO_3 is used. In this case, however, rate of oil production changes very sharply with the alkali content of the catalyst. A catalyst containing 4 parts K_2CO_3 and a catalyst containing no H_3BO_3 have high activities even at lower temperatures, with rates of oil production of 116 gm. per m.³ and 84 gm. per m.³, respectively, at 220°. The optimum amounts of Cu and kieselguhr to be added are 25 parts and 50–125 parts, respectively.

KODAMA, S., TARAMA, K., TAKAZAWA, T., FUJITA, K., TEJIMA, T., ITO, S., AND YOKOMAKU, Y. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. VII. Effect of Temperature .on Synthesis with Cobalt Catalysts. See abs. 1918.

――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. VIII. Effect of Composition of the Synthesis Gas on Iron Catalysts. See abs. 1919.

――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. IX. Effect of Addition of Diatomaceous Earth on Iron Catalysts. See abs. 1920.

――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. X. Effect of Various Carriers on the Iron Catalysts. See abs. 1921.

――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XI. Comparative Study of the Synthesis Under Normal Pressure and Other Pressures. See abs. 1922.

――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XII. Effect of Pressure. See abs. 1923.

――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XIII. Effect of Temperature at Constant Pressure. See abs. 1924.

――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XIV. Effect of Various Carriers and Promoters. See abs. 1925.

――――. Synthesis of Gaseous Hydrocarbons From Carbon Monoxide and Hydrogen. XV. Summary of the Studies on the Synthesis Under Pressure. See abs. 1926.

1930. KODAMA, A., FUNABASHI, W., HASHIMOTO, G., HIRAO, T., TAHARA, H., MATSUMURA, A., KATO, J., AND TARAMA, Y. Process Development in the Hydrocarbon Synthesis to 1941. Bureau of Mines Inf. Circ. 7593, 1951, 41 pp.

Report compiled from Japanese documents on the investigation of the Fischer-Tropsch process. Some of the results are summarized as follows. (Experiment 17.) Using a Co catalyst in a water-cooled converter (designed for synthesis gas throughput of 100 m.³ per hr.), a 2-week run was carried out successfully. Over a reaction temperature range 200°–215° and at an average gas throughput of 79.6 m.³ per hr., the following average yields were obtained at an average apparent contraction of 56.2%: 168 ml. H_2O, 86 ml. of primary liquid products (oil), and 7 l. of gasol per m.³ of synthesis gas. Correcting these results for the 15.5% of.inerts in the synthesis gas, an actual contraction of 66.5% was obtained and the yields were increased to 199 ml. H_2O, 102 ml. oil, and 8 l. gasol per m.³ of pure 2 H_2 : 1 CO synthesis gas. The catalyst was constituted as follows: 100 Co : 10 Cu : 5 ThO_2 : 2.5 U_3O_8 : 125 diatomaceous earth. The results suggest that commercial synthesis of gasoline and hydrocarbon oils in a water-

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cooled converter may be economically feasible. Preparation and purification of synthesis gas is described. Using the same converter and an Fe catalyst (experiment 18) (a mixture of two catalysts of different Cu contents—100 Fe: 25 Cu (12.5 Cu): 2 Mn: 20 H_3BO_2: 4 K_2CO_3: 125 kieselguhr), a 1-month run was made. The average operating results compared favorably with that using Co catalyst:

	Cobalt	Iron
Operating time, days	14	25
Initial temp., °C	202	235
Final temp., °C	211	238
Synthesis gas used, m.³	26,729	56,255
Total oil formed, l.	2,288	4,203
cc. per m.³ synthesis gas	86	75
cc. per useful gas	102	86
cc. per m.³ $H_2 + CO$	139	180

1931. KOENIG, A., AND WEINIG, R. [Formation of Formaldehyde From Water Gas in the Electric Glow Discharge.] Festschrift 100-Jähr. Bestehen Tech. Hochschule zu Karlsruhe, 1925, pp. 525–530; Chem. Zentralb., 1926, II, p. 2134; Chem. Abs., vol. 21, 1927, p. 3834.

Treatment of mixtures of CO and H_2 by the glow current leads to gaseous, liquid, and solid products of varying composition, among which H_2O, CO_2, HCO_2H, HCHO, and glycolaldehyde were identified (see abs. 2130). In attempts to determine the optimum conditions for HCHO formation, it was proved that with a current of gas, the products are adsorbed and adhere to the walls as a result of electrophoresis. To avoid their enrichment with undesirable reaction products, the walls of the Siemens tube were continuously or periodically rinsed with water. In this way it became possible to obtain HCHO as the chief product of the action of the glow discharge on water gas, so that up to 77% of the gas treated was recovered as HCHO. The maximum yield of HCHO was obtained when the incoming gas contained 46% CO by volume. Calculated on a basis of the electric energy consumed, the yield was 2 gm. of HCHO per kw.-hr.

1932. KOETSCHAU, R. [Nature and Occurrence of Natural Petroleums, Their Chemical Relationship to Each Other and to the Distillation Products of Coal.] Brennstoff-Chem., vol. 8, 1927, pp. 273–288; Chem. Abs., vol. 22, 1928, p. 1464.

Review of the literature on chemical composition of petroleum and a discussion of the theories on its origin. A possible connection is assumed between the formation of natural petroleum and of synthetic petroleum from gas by the Fischer-Tropsch process.

1933. KOHLE UND ERZ. [Diesel Fuel From Coal.] Vol. 36, May 4, 1939, p. 278.

1934. ———. [Oils and Fats From Coal in Germany.] Vol. 36, No. 23, 1939, pp. 640–641; Coke Smokeless-Fuel Age, vol. 2, 1940, p. 71.

From the standpoint of oil and fat production, the Fischer-Tropsch synthesis is important. The paraffin-bearing intermediate product gatsch coming between Diesel oils and solid paraffin is an excellent material from which to start the synthesis of fatty acids. Catalytic oxidation is effected at low temperatures, up to 120° C, and fatty acids are derived from which a whole series of soaps can be prepared. The fatty acids production of Germany is now about 30,000–40,000 ton per yr. and is increasing.

— — KÖHLER, G. See abs. 2435.

1935. KOHLHAAS, R., AND MEYER, W. F. [Formation, Stability and Structure of Nickel Carbide.] Metallwirtschaft, vol. 17, 1938, pp. 786–790; Chem. Abs., vol. 32, 1938, p. 7870.

Addition of C to Co-free Ni, in the form of powder or wire from benzene vapor, water gas, or illuminating gas at temperatures ranging 230°–730° shows that only Ni_3C is observable, which is formed from 240°

up to 530°–580°. Tempering experiments in a vacuum show the Ni_3C formed above 420°–500° to be metastable. The separation of C increases very much with increasing temperature; probably it is due to the diffusion equilibrium of the gases used and their decomposition products. X-ray pictures show that Ni_3C can have no hexagonal symmetry but that a rhombic structure of the compound and hence its isomorphy with Fe_3C and Co_3C is very likely.

1936. KOHLSCHÜTTER, H. W., AND LOHNES. K. [Preparation and Transformation of Iron Nitride.] Ztschr. anorg. Chem., vol. 255, 1947, pp. 73–78; Chem. Abs., vol. 43, 1949, p. 2744.

Preparation of the nitrides of Fe by reaction of Fe with NH_3 and the catalytic decomposition of NH_3 with the intermediate formation of Fe_2N.

1937. KOHLSCHÜTTER, V., AND NÄGELI, A. [Topochemical Reactions. Formation of Carbon on Contact Substances.] Helv. Chim. Acta, vol. 4, 1921, pp. 45–76; Chem. Abs., vol. 15, 1921, p. 2767.

Study was made of the nature of the C deposited upon electrolytic films of Co. Ni, Fe, and Ag and upon powders of these metals by the reaction $2 CO = C + CO_2$, at about 500°. The supporting metal upon which the catalytic metals are electrolytically deposited influences the amount of C formed, it being greater when the support is Pt, and less when it is Ag or Cu. The nature of the catalytic metal determines specifically the method of deposition and the amount and the characteristics of the C. In the case of smooth Co, Ni, and Ag deposits, the C is not deposited visibly upon the surface but in the interior of the metallic film and appears as an unweighable film when the metal is dissolved in acid. In the case of Fe, however, the C forms a deep-black surface deposit. Co affords the largest C deposit, then Ni, Fe, and Ag. The C deposited on Co is strongly graphitic: on Ni also graphitic, but somewhat more easily oxidizable; on Fe more sooty, and still more easily oxidizable; and on Ag very small in amount and difficult to oxidize. On dark, lusterless deposits the C is deposited visibly on the surface, as was the case with smooth deposits of Fe; and it is more easily oxidized than C deposited within the metallic layer. The amount of C produced by metallic powders was large and almost inseparably associated with fine particles of the metal.

1938. KOHN, S. Theory of the Water-Gas Process. Jour. Ind. Eng. Chem., vol. 14, 1922, pp. 69–72; Chem. Abs., vol. 16, 1922, p. 634.

Kohn discusses the 10 possible and the 3 probable combinations of reactions that can be used to explain the water-gas process. Demonstration is made of a possibility of drawing conclusions from the composition of the resulting gases to the actual procedure of the reactions. The applicability of the principles outlined is tested on a series of 9 observations published by Bunte and Harries, and their application to catalytic observations is discussed.

KOIDE, H. See abs. 1877, 1889.

1939. KÖLBEL, —. [Hydrocarbon Synthesis With an Iron Catalyst.] TOM Reel 178, Sept. 13, 1940, frames 2,627–2,642; Bureau of Mines Transl. T-468, Dec. 28, 1948, 21 pp.; PB 97330t2.

Lecture pointing out advantages in substituting Fe as the catalytic element in place of Co. Brief discussion of the problems met during the development of the Fe catalyst, and some results of the investigation. Some suggestions are made for carrying out the synthesis with powdered-Fe catalyst in the liquid phase.

1940. KÖLBEL, H. [Content of Cobalt and Diatomaceous Earth in Gasoline Synthesis Catalysts.] FIAT Reel K-30, frames 7454–7467, Mar. 9, 1938; PB 73,587.

Test results on the influence of the Co and diatomaceous earth content on the efficiency of gasoline synthesis catalysts are discussed. It was found that a reduction of the Co and its replacement by a correspondingly larger quantity of diatomaceous earth exceeding the ratio 1 : 1 diminishes the yield of liquid products. Furthermore, with a constant quantity of CO and a constant flow velocity of the gas, an increase of the Co : diatomaceous earth ratio beyond 1 : 1 up to 1 : 1.2 does not improve the catalyst. By the use of catalysts poorer in diatomaceous earth the capacity of the catalyst space increases by 40–60%, as compared with catalysts now in use.

1941. ———. [Diesel-Fuel Mixtures From Bituminous-Coal Tar Oil.] Oel u. Kohle Erdoel Teer, vol. 14, 1938, pp. 1042–1049; Brennstoff-Chem., vol. 20, 1939, p. 92; Chem. Abs., vol. 33, 1939, p. 7989.

By heat pretreatment with and without pressure and catalyst (abs. 2301) mixtures of tar oil and Kogasin II yield fuels suited for high-speed use, with desired ignitability, carbonization, storage stability, and miscibility characteristics in motor and road tests.

1942. ———. [Importance of the Fischer-Tropsch Synthesis for the Production of Domestic Diesel Fuels. I.] Brennstoff-Chem., vol. 20, 1939, pp. 352–355; Chem. Abs., vol. 34, 1940, p. 7573.

Properties of Kogasin II and the possibilities of motor uses, particularly in diesel mixtures.

1943. ———. [Importance of the Fischer-Tropsch Synthesis for the Production of Domestic Diesel Fuels. II.] Brennstoff-Chem., vol. 20, 1939, pp. 365–369; Chem. Abs., vol. 34, 1940, p. 7573.

Mixtures of Kogasin II with bituminous coal-tar oil, especially tar oils obtained from carbonization processes employing offtake from within the coal charge, and high-pressure hydrogenated oils prepared from coal, coal tar, and coal extracts are discussed. Depending upon ignition characteristics, 40–55% Kogasin II can be used to make fuel mixtures of 65–85 cetene no. and equal to the petroleum fuels in ignitability, resistance to coke formation, and completeness of combustion. Unrefined tar oils destroy the storage stability of the mixtures, as well as their motor values.

1944. ———. [Synthesis of Lubricating Oil Through Alkylation of Naphthalene.] Erdöl u. Kohle, vol. 1, 1948, pp. 308–318; Chem. Abs., vol. 43, 1949, p. 4454.

Method is based on the condensation of chlorinated paraffin hydrocarbons obtained from the Fischer-Tropsch synthesis with naphthalene by means of the Friedel-Crafts reaction. Kogasin $d_{20} = 0.77$; boiling point, 280°–320°; Cl 20.9% was superior to a similar petroleum fraction as base stock. Physical properties of various synthetic oils are given; d_{20} of synthetic motor oil is approximately 0.925, in contrast to petroleum oils, density has no significance as a criterion of quality for synthetic oils. Gasoline- Diesel- and steam-engine tests showed a superiority of the synthetic oils over good quality natural oils. Includes a plant diagram.

———. See abs. 409, 1040, 1041, 1336, 1837.

1945. KÖLBEL, H., AND ACKERMANN, P. [Hydrogenation of Carbon Monoxide in Liquid Medium.] Angew. Chem., vol. 61, 1949, p. 38.

Carrying out of the Fischer-Tropsch synthesis in a liquid medium is claimed to offer considerable advantages.

1946. ———. Hydrogenation of Carbon Monoxide in a Liquid Medium. Bureau of Mines Transl. K-10, 1949, 19 pp.

Paper read at a meeting of German Chemical Society, September 1948. Synthesis in the liquid phase with a suspended catalyst eliminates completely the

disadvantages of synthesis in the vapor phase, such as local overheating of the catalyst, CH_4 formation, hydrocarbon deposition, plugging of the reactors, nonuniform utilization of the catalyst, imperfect cooling, complicated filling and emptying of the reactors, and limitations upon the reactor capacity. The process has been studied chiefly with Fe catalyst and has been developed to the industrial stage and results in higher yields than obtained in the vapor phase with the same CO conversion of up to 175 gm. of hydrocarbons per m.³ $CO + H_2$ because of the suppression of CH_4 formation. H_2O is formed as a primary product of the reaction upon the Fe catalyst as well as upon the Co catalyst and is converted to CO_2 and H_2 with the CO of the synthesis gas. It is possible to conduct the synthesis over Fe catalyst entirely by way of formation of water and over Co catalyst completely by way of CO_2 formation. It is therefore possible to obtain good yields with CO-rich gases, water gas, or H_2-rich gases with Fe catalyst by properly adjusting the operating conditions. It is shown for the first time that during CO hydrogenation the chain length of the higher molecular weight saturated and unsaturated aliphatic hydrocarbons can be increased. Operating in liquid phase permits the conversion up to 73% of the paraffin hydrocarbons to solid paraffins, so that 1 m.³ of $CO + H_2$ will produce 152 gm. of paraffin boiling above 320°, of which 95 gm. are formed during CO hydrogenation, and 57 gm. by the lengthening of the C chain.

1946a. ———. Hydrogenation of Carbon Monoxide in Liquid Phase. Proc. 3d World Petrol. Cong., The Hague, May–June 1951.

Using a finely-divided Fe catalyst in the fluidized state, certain advantages were obtained which were claimed to largely meet economy requirements for the Fischer-Tropsch process. Advantages over fixed-bed operation included faster removal of reaction heat, reduction of CH_4 formation and C deposition, reduction of reactor choking, and utilization of a gas space velocity 4–8 times higher. Using larger reactors and smaller cooling surfaces the relative weight of the synthesis furnace as well as capital service charge were said to be reduced to ¼.

———. Reaction Mechanism of the Fischer-Tropsch Synthesis. IV. Molecular Size of the Aliphatic Hydrocarbons From the Catalytic Hydrogenation of Carbon Monoxide. See abs. 1950.

1947. KÖLBEL, H., AND ENGELHARDT, F. [Reaction Mechanism of the Fischer-Tropsch Synthesis. I.] Erdöl u. Kohle, vol. 2, 1949, pp. 52–59; Chem. Abs., vol. 43, 1949, p. 4828.

Proposed mechanisms explaining the formation of CO_2 and H_2O by Fe and Co catalysts, respectively, are reviewed and the action of these catalysts in the water-gas reaction is studied. An Fe catalyst of composition 100, Fe; 0.5, Cu; 0.25, K_2CO_3 was used. Initial experiments were conducted with four different contact conditions: Carbidic, 24-hr. treatment with CO at 270° (I); metallic, 24-hr. treatment of (I) with electrolytic H_2 at 270° (II); oxidic, reduction of catalyst with H_2 at 270° (III); synthesis, treatment for 100 hr. at 1 atm. at 230°, CO: $H_2O = 1:2$, space velocity 100, (IV). A graph of time, total 24 hr., versus conversion of CO at 240°, CO: $H_2 = 1:1$, space velocity = 100, gives almost a straight line for (I) near equilibrium; (IV) runs parallel to (II) at a lower level; (III) is inactive at this temperature; and (I) is rapidly approaching (IV). Results at 240°, $CO + H_2O = 3:1$ and space velocity = 100, show that (I) and (II) have approached each other within the first 100 hr. and then run concurrently for more than 400 hr. Analysis of (I) for total C, elemental C, carbidic C, and unoxidized Fe, respectively, before test: 14.2, 7.35, 6.85, 62.7; after: 16.2, 12.0, 4.2, 57.3. Similar

results for (II) are before; 7.0, 7.0, 0.0, 67.1: after; 19.0, 14.2, 4.8, 56.9. Results indicate that initially (II) is more active than (I), but that finally both attain the same activity and carbide concentration. Method for analysis is based on the fact that the velocity of ion exchange is a function of the carbide–C content in such a way that with increasing carbide–C the permutation velocity decreases; Hg⁺⁺ ions were used. Carbide–C was determined by difference of total C before and after treatment with H₂ at 270°. A highly reactive, commercial Co–Th–Mg catalyst with 100% kieselguhr was treated as follows: By reduction of a precipitated catalyst with H₂ at 450° (V); 24-hr. treatment of (V) with CO at 270° (VI); active use for 150 hr. (VII). (V) is by far the best, conversion close to equilibrium; (VI) is the poorest; (VII) midway between the two. For CO : H₂O=1 : 1 and space velocity=100, 180° was the lower limit of conversion for both Fe and Co catalysts. This is important in connection with the fact that the optimum synthesis for the Co catalyst is below 180° while that for Fe is considerably higher, which may explain that in the former O₂ from CO can escape in the form of H₂O. Experiments with a Co catalyst showed that lowering the space velocity from 100 to 10 at 180° and changing the H₂ : CO ratio from 2 : 1 to 2 : 3.55. H₂O concentration decreased progressively and an almost parallel increase of CO₂ resulted. Division of the Fe catalyst into four portions separated by layers of CaCl₂ (230°, space velocity 100) resulted in a progressive increase of H₂O formation and a parallel decrease of CO₂ concentration. These results are in disagreement with the opinion advanced by Craxford (see abs. 638). A working hypothesis for the mechanism is proposed.

1948. KÖLBEL, H., ACKERMANN, P., JUZA, R., AND TENTSCHERT, H. [Reaction Mechanism of the Fischer-Tropsch Synthesis. II. Investigation of Iron Catalysts in the Hydrogenation of Carbon Monoxide.] Erdöl u. Kohle, vol. 2, 1949, pp. 278-285; Chem. Abs., vol. 43, 1949, p. 8117.

Fe catalysts prepared from Fe (NO₃)₃, initially α-Fe₂O₃, promoted with Cu (0.001–0.16%), K₂CO₃ (0.0–0.25%), and BaCO₃ were investigated analytically, catalytically, magnetically, thermomagnetically, by means of X-rays, and by adsorption measurements. It was found that the milder the treatment during preparation, the more imperfect the α-Fe₂O₃ lattice and the greater the surface development. Promotion with Cu or alkali had no influence on the state of crystallization. After exposure to synthesis, the catalyst consisted principally of magnetite (Fe₃O₄) and always contained Fe carbide. No free Fe was present. Whether Cu or K was built into the magnetite lattice could not be decided. Below 5%, Cu could not be detected by means of X-ray analysis. Above 5% it was present in the elementary state. In active catalysts, the system Fe–C is a function of the original composition and the conditions of catalysis (CO–H₂). A labile carbide (Curie temperature, 220°) appears initially during synthesis and is stable only to about 290°. After longer synthesis exposure, a second thermally stable carbide (Curie temperature between that of cementite Fe₃C and that of Fe₂C) either replaces the first or is formed in addition. High alkali content, higher gas pressures, and CO content in combination with longer synthesis exposure favor the formation of Fe₂C (Curie temperature 250°) stable up to 400°. Since even the most labile of the 3 carbides had virtually no influence on the catalyst activity, it is concluded that Fe carbide is not the important intermediary it was thought to be previously. For confirmation, see abs. 2009.

1949. KÖLBEL, H., AND LANGHEIM, R. [Reaction Mechanism of the Fischer-Tropsch Synthesis. III.

Investigation of the Carbides Formed in the Hydrogenation of Carbon Monoxide on Iron Catalysts.] Erdöl u. Kohle, vol. 2, 1949, pp. 544-550; Chem. Abs., vol. 44, 1950, p. 3235.

Purpose of the work reported in this paper was to examine the carbide theory of CO hydrogenation and to explain the carbide found by thermalmagnetic examination on used Fe catalysts. Of further interest was the effect of the promoters of Fe catalyst, alkali and Cu, on carbide formation. A review of the work of other investigators on the formation of Fe carbides is presented. In the treatment of pure, paramagnetic γ-Fe₂O₃ with CO at 265° a carbide Fe₂C is obtained. Beside this there is a separation of elementary C. The stability of the Fe₂C, which results in a certain manner from the speed of hydrogenation of the carbide–C, depends upon the raw material and its previous history as well as upon the conditions surrounding its preparation. Alkali hastens the formation of carbide- and elementary C. Cu accelerates the formation of carbide- but exerts a negative effect on the formation of elementary C. It also hastens the reduction of the Fe catalyst in carbide formation and CO hydrogenation. In the presence of both alkali and Cu, the speed of formation of carbide- and of elementary C undergoes a further, quite considerable increase. The X-ray diagram of Fe₂C agrees well with that found by G. Hägg, and the Curie point lies at about 240°–250°. The formation of a well-defined carbide and the synthesis reaction are not 2 consecutive but 2 parallel occurring reactions, which have their common starting point in the activation of the CO, which in one case leads to carbide formation and in the other to hydrocarbons. Alkali catalyzes both reactions directly, Cu catalyzes indirectly through the acceleration of the reduction of Fe₂O₃.

1950. KÖLBEL, H., AND ACKERMANN, P. [Reaction Mechanism of the Fischer-Tropsch Synthesis. IV. Molecular Size of the Aliphatic Hydrocarbons From the Catalytic Hydrogenation of Carbon Monoxide.] Brennstoff Chem., vol. 31, 1950, pp. 10–14; Chem. Abs., vol. 44, 1950, p. 3697.

When higher-molecular liquid aliphatic hydrocarbons (C₁₅–C₁₉ hydrocarbons from Kogasin) are introduced into the Fischer-Tropsch synthesis, they form solid hydrocarbons by chain lengthening under synthesis conditions that normally lead to the predominant formation of high molecular hydrocarbons, solid at normal temperatures. The rate of this chain lengthening is directly related to the building up activity of the catalyst. As regards the synthesis-gas mixture (used along with the higher hydrocarbons), 45–57 gm. of solid hydrocarbons are formed per m.³ of the CO–H₂ mixture. Two different Kogasin fractions were used, containing 2 and 11% of olefins, respectively. No difference could be noted as to their reactivity. Reviews theories as to the reaction mechanism.

1951. KÖLBEL, H., AND ENGLEHARDT, F. [Reaction Mechanism of the Fischer-Tropsch Synthesis. V.] Angew. Chem., vol. 61, 1949, p. 448; Chemie-Ing. Tech., vol. 22, 1950, pp. 97–104; Chem. Abs., vol. 44, 1950, p. 5566.

Paper presented at the annual meeting of the German Chemical Society in September 1949. After a brief review of the empirical development of the synthesis, the carbide theory of Fischer is thoroughly examined. The composition of the catalyst in respect to operating conditions as well as to the synthesis of higher hydrocarbons is discussed both from the standpoint of previous work and from more recent conceptions. It is shown that the carbide theory no longer stands up against experimental proof. Activated adsorption is put forward as the basis for a new working hypothesis, and the possibility of a uniform method

of examination of all CO hydrogenation processes is discussed.

1952. ———. [Reaction Mechanism of the Fischer-Tropsch Synthesis. VI. Function of Water Vapor in the Hydrogenation of Carbon Monoxide.] Erdöl u. Kohle, vol. 3, 1950, pp. 529–533; Chem. Abs., vol. 45, 1951, p. 2177.

This paper was presented at the 3d meeting of Die Deutsche Gesellschaft für Mineralölwissenschaft und Kohlechemie, September 1950. CO₂ formation on the Fischer-Tropsch catalysts results from a secondary reaction of CO with primarily formed H₂O vapor. The result of this conversion reaction is important in the choice of synthesis conditions. The effect of temperature upon the reaction has been previously determined, and now proof is made of the influence of space velocity on the conversion of CO with water vapor, especially in the presence of Fe catalyst. The results obtained permit of predicting the CO : H₂ ratio for the synthesis and the space velocity to be chosen for obtaining satisfactory yields; they offer further some criterion for the most favorable synthesis gas composition for a given space velocity and temperature. Determination of the speed of reaction of the CO conversion in a static system at temperatures down to 85° supposes a reaction of the first order, which may rest upon the dissolution of the adsorption complex of CO with H₂O on the catalyst surface. By using a H₂-rich gas and space velocities of about 100, at normal pressure above 180° an oxidation of the catalyst by the water vapor formed during the synthesis occurs, in case a definite relation is maintained between the partial pressures of the CO and H₂O in the reaction gas. Under these conditions the outer catalyst layers deteriorate through oxidation by water vapor. The CO conversion is then to be considered not only as a troublesome side reaction, but it acts under certain conditions as a protector of the Fe catalyst against oxidation. In the hydrocarbon synthesis on Fe catalysts under normal pressure, the space velocity must either be chosen so high and the temperature so low that neither CO conversion nor catalyst oxidation occurs or the CO content of the synthesis gas must be so high that even in the outer catalyst layers enough CO is present to react with the water vapor with satisfactory velocity. In practice these conditions should exist in proper combination.

1953. ———. [Synthesis of Hydrocarbons and Oxygen-Containing Compounds From Carbon Monoxide and Water Vapor.] Brennstoff-Chem., vol. 32, 1951, p. 150; Chem. Abs., vol. 45, 1951, p. 7333.

In addition to the usual reaction of CO and H₂ to form hydrocarbons, the reaction $3\ CO + H_2O \rightarrow (CH_2) + 2\ CO_2$ is important in forming hydrocarbons. While this reaction proceeds at normal pressure under suitable conditions, it is favored by high pressure and a temperature 200°–300° in presence of a highly active catalyst. Yields of 195 gm. (theoretical 208 gm.) hydrocarbons per standard cu. m. of CO were secured, and a wide variety of O-containing compounds was formed, including aldehydes, alcohols, acids, oxy acids, etc., CO-containing gases can be used, as well as pure CO.

1953a. ———. [Synthesis of Hydrocarbons and Oxygenated Compounds From Steam and Carbon Monoxide.] Brennstoff Chem., vol. 33, 1952, pp. 13–21; Erdöl u. Kohle, vol. 5, 1952, pp. 1–9; Angew. Chem., vol. 64, 1952, pp. 54–58; Chem. Age, vol. 66, 1952, pp. 375–376.

CO and H₂O can be converted in a single step to paraffin hydrocarbons and oxygenated compounds using catalysts of group 8 and either standard or high pressures and temperatures 210°–260°, space velocity 1,000 or more. H₂O : CO<0.5. Conversion of H₂O and CO were both over 90%. Yields up to 216 gm. hydrocar-

bons and oxygenated compounds per m.³ CO were obtained. The reacting elements must be in strictly definite and somewhat narrowly defined limits. Thus, for hydrocarbons: $H_2O + 3\ CO \rightarrow (-CH_2-) + 2\ CO_2$ and for alcohols (ethyl) : $3\ H_2O + 6\ CO \rightarrow C_2H_5OH + 4\ CO_2$. Another important factor in maximum efficiency is the space velocity which is governed by reaction rate at the catalyst surface and involves the duration of contact by the reacting elements. Effect of pressure is discussed with pressures up to 100 atm. Temperature must be adjusted for maximum catalyst activity, but not so high as to cause undesirable side reactions. With a freshly reduced Fe catalyst and normal pressure at 200°, the water gas reaction predominated; yet even with a slight rise to 210° the CO conversion was 90%, and rose to 93–97% at 250° after which it slowly declined with further increase of temperature. CH₄ formation increased beyond 240°, and from this point production of hydrocarbons was no longer parallel with CO conversion. Cheap industrial gases with low CO content, such as generator and furnace gases, can be used without serious inconvenience. Products are mainly saturated and unsaturated paraffins with olefins ranging 35–60% and up to solids in the homologous series. Alcohols may also be produced, especially at pressures >30 atm., with minor amounts of aldehydes, fatty acids and esters. EtOH predominates. The % compositions of the products obtained at 0 and 100 atm. at 235°–238° are tabulated. (See also abs. 1953.)

———. [Reaction Mechanism of the Fischer-Tropsch Synthesis. V.] See abs. 1951.

———. [Reaction Mechanism of the Fischer-Tropsch Synthesis. VI. Function of Water Vapor in the Hydrogenation of Carbon Monoxide.] See abs. 1952.

KÖLBEL, H., AND LANGHEIM, R. [Reaction Mechanism of the Fischer-Tropsch Synthesis. III. Investigation of the Carbides Formed in the Hydrogenation of Carbon Monoxide on Iron Catalysts.] See abs. 1949.

1954. KÖLBEL, H., AND ULLMANN, D. [Greases From the Initial and Final Fatty Acid Fractions of Paraffin Oxidation.] Erdöl u. Kohle, vol. 3, 1950, pp. 16–21; Chem. Abs., vol. 44, 1950, p. 4234.

Initial (4–9 C atoms, equivalent weight 110–130) and final (more than 20 C atoms, equivalent weight 310–360) fatty acid fractions from the paraffin oxidation of the Fischer-Tropsch fraction of 320°–450°, ordinarily waste products, formed superior Ca and Na greases when mixed in a 40 : 60 ratio. The low-molecular fraction contributed greatly to better storage stability (no change after 8–10 years) and in combination with Na was responsible for increase in drip point of the mixture. Substitution of Na acetate and Na formate for the low-molecular acids produced an increase in drip point similar to that obtained by the low-molecular fraction. A theoretical explanation of this behavior is attempted. Bearing-test results were satisfactory.

KÖLBEL, H., ACKERMANN, P., JUZA, R., AND TENTSCHERT, H. [Reaction Mechanism of the Fischer-Tropsch Synthesis. II. Investigation of Iron Catalysts in the Hydrogenation of Carbon Monoxide.] See abs. 1948.

1955. KÖLBEL, H., ACKERMANN, P., RUSCHENBURG, E., LANGHEIM, R., AND ENGELHARDT, F. [Fischer-Tropsch Synthesis on Iron Catalysts. I., II. Induction of Iron Catalysts, Behavior During Synthesis, and Results Obtained in Various Synthesis Processes.] Chemie-Ing. Tech., vol. 23, No. 7–8, 1951, pp. 153–157, 183–189.

Comprehensive review of previous investigations. Discusses influence of surface improvement and com-

position as well as the role of promoters and of Fe carbides on the activity of the catalyst, the preparation of precipitated catalysts, the induction of the catalyst, its reaction mechanism and behavior in the synthesis, and the results of various synthesis processes. Fixed-bed vapor-phase and liquid-phase operation is considered also.

KOLLWITZ, J. *See* abs. 711.

1956. KOMAREWSKY, V. I. Production of Synthetic Liquid Fuel From Natural Gas. Petrol. Refiner, vol. 24, No. 5, 1945, pp. 96-98; Petrol. Eng., vol. 16, No. 12, 1945, pp. 202, 204, 206.

Fischer-Tropsch synthesis is reviewed with brief description of the products—gasoline, diesel oil, paraffins, and lubricants. The progress of the process was accelerated by the discovery of the middle-pressure synthesis in 1936. At pressures of 75-220 p. s. i., an optimum yield of solid plus liquid hydrocarbons was obtained. The chief advantage was that loss in catalyst activity was decreased. Whereas the yield dropped from 7.7 to 5.9 lb. per 1.000 cu. ft. in normal-pressure synthesis in 4 weeks, the middle pressure synthesis produced 8.9 lb. initially, and still was above 5.9 lb. after 26 weeks of operation. This synthesis has been performed with Co and Fe catalysts: Ni catalysts deteriorate rapidly owing to formation of Ni carbonyl. In 1938 it was found that Ru catalyst at high pressure produced solid hydrocarbons more effectively than any other metal of the 8th group. At 1.500 p. s. i. pressure and 383° F., 5.9 lb. of paraffin wax and 3 lb. of oil were obtained per 1.000 cu. ft. of synthesis gas with no appreciable change in the activity of the catalyst in a 6 months test. By solvent extraction of a solid paraffin obtained in this way, a wax was obtained with a melting point of 270°-273° F. and with a molecular weight of 23,000. Recently 2 new syntheses have been announced, naphthene synthesis and isosynthesis; details, however, have not been disclosed. It is implied that gasoline of higher octane numbers is produced; naphthenes and aromatics and isoparaffins, respectively, are produced. In the latter case the C₄ fraction from the process contains 90% of isobutane. Future developments in the Fischer-Tropsch process must proceed in the following directions: (a) Development of a S-resisting catalyst; (b) utilization of CO-H₂ mixtures of various composition; (c) synthesis of branched-chain hydrocarbons. The last can probably be attained by developing a complexaction catalyst combining the hydrogenation, polymerizing, and isomerizing ability.

—————. *See* abs. 2824.

1957. KOMAREWSKY, V. I., AND RIESZ. C. H. Fischer-Tropsch Synthesis and the Gas Industry. Petrol. Refiner, vol. 23, No. 11, 1944, pp. 415-422.

Reviews of the development of the process from the beginning to the present. A reaction mechanism is proposed, which postulates that the function of the catalyst is to provide a hydrogenating-polymerizing surface whereby CO is converted to CH₂ at the catalyst surface, and this is polymerized to hydrocarbons containing more than 1 C atom. Poisoning of the catalyst by S is explained on the basis of this mechanism. The process is of potential value to the gas industry, since it offers the possibility of converting off-peak gas production to valuable products. The costs of the process must however first be lowered to make it economical. Research should be directed toward the following objectives: Develop more active catalysts, which will operate at shorter contact periods; produce a catalyst capable of directing the reaction toward a specific product, for example, iso-paraffins; obtain a S-resistant catalyst having a tolerance of at least 2-4 grains of S per 100 cu. ft.; develop a process that will utilize a 1:1 mixture of CO : H₂.

1958. —————. Fischer-Tropsch Synthesis and the Petroleum Industry. Nat. Petrol. News, Tech. sec., vol. 37, 1945, pp. R-97-104.

Review of historical development and various theories of the mechanism of the reaction.

1959. KOMAREWSKY, V. I., RIESZ, C. H., AND THONOS, G. Aromatization of Fatty Alcohols. Jour. Am. Chem. Soc., vol. 61, 1939, pp. 2525-2527; Chem. Abs., vol. 33, 1939, p. 8580.

Under the action of a mixed CrO₂-Al₂O₃ catalyst, fatty alcohols undergo a complex reaction involving dehydration, Al₂O₃, dehydrogenation and cyclization, CrO₃, producing aromatic hydrocarbons. It is proposed to name this type of mixed catalysts complex-action catalysts. The reaction of aromatization is of the first order and formula. $K=2.303/t \log a1, a-x$, where t is time, a the amount taken into the reaction and x the amount of product in %, can be applied. The energies of activation are calculated. Heptyl alcohol at 450° gives 7.8% of PhMe and at 500° 58-66% PhMe, calculated from $n \frac{25}{D}$ and from H₂ of the gases evolved, Pr₂CHOH at 468° gives about 7% and at 480° about 13% PhMe; hexyl alcohol at 467° gives 38% and at 500° 38% PhMe; octyl alcohol at 475° gives 3% PhMe, 4.5% PhEt. 7% of the xylenes, and 32.7% of higher boiling aromatics. The gases evolved consist of O₂, CO, CO₂, and H₂. A table gives the amount of alcohol dehydrated, dehydrogenated, and cyclized.

1959a. KOMATSU, S., AND KURAKU. H. Catalytic Action of Nickel-Magnesium on the Reaction Between Methane and Steam. Jour. Chem. Soc. Japan, vol. 63, 1942, pp. 1.551-1.554; Chem. Abs., vol. 41, 1947, p. 3.267.

It is found that 91-95% CH₄ is decomposed by steam at 650°-700° in the presence of Ni-Mg catalyst. The best catalyst is prepared as follows: Ni(NO₃)₂ and Mg(NO₃)₂ are dissolved in H₂O (Ni : Mg=9 : 1). The solution is absorbed by the grains of pumice stone and calcined at 400° and reduced by H₂.

KOMAZAWA, S. *See* abs. 1927, 1928, 1929.

KOMIYAMA, D. *See* abs. 3314, 3315.

1960. KÖNIG, E. [Synthetic Oils From Coal Gasification Products at Ordinary Pressure.] Teer. vol. 24, 1926, pp. 385-387; Brennstoff-u. Wärmewirt., vol. 8, 1926, pp. 228-229; Chem. Abs., vol. 20, 1926, p. 3557.

Noncritical review of Fischer's recent work on oils from water gas. (*See* abs. 1021.)

1961. KÖNIG, H. [Smallest Ferromagnetic Elementary Size of Iron.] Naturwissenschaften, vol. 33, 1946, pp. 71-75; Chem. Abs., vol. 41, 1947, p. 7177.

Review in some detail of history of ferromagnetism and various methods used to determine the size of the elementary Fe magnet. The author's method, in which a collodion film with attached Fe layer is brought between the poles of a magnet and the magnetism determined by Farraday effect, rotation of polarized light, is described more specifically. Differences were found for different types of Fe precipitates. From 20 different Fe films it was found that the smallest mean crystal size to give measurable rotation; that is, ferromagnetism, is 10-12 Å. With γ-Fe₂O₃, ferromagnetism does not begin until the particles are 30-40 Å. In both cases, this indicates the presence of at least 64 elementary cell units.

1962. KONOBEYEVSKI. S. [Solid Solution of Iron in Graphite.] Ztschr. Krist., vol. 72, 1929, pp. 381-397; Chem. Abs., vol. 24, 1930, p. 1011.

Diffraction patterns from some natural graphites were duplicated in samples of graphite heated with Fe. Solid solution of Fe in the graphite occurs with the probable formation of Fe₂C. The presence of

superstructure lines in the pattern indicates a regular distribution of the Fe atoms.

1963. KOPPENBERG, H. [Mineral Oil From Coal.] Vierjahresplan, vol. 1, 1937, pp. 271-277.

Technical and economic aspects of the production of synthetic motor fuels are discussed, with special reference to the Bergius high-pressure and the Fischer-Tropsch synthetic processes by means of which Germany is to be made independent of foreign oil supplies.

—————. *See* abs. 3088.

1964. KOPPERS REVIEW. Chemistry and Economics of the Fischer-Tropsch Process. Vol. 2, No. 3, 1937, pp. 99-139.

Describes the process and its products. Gives analyses of the lubricants obtained from olefins produced in the process and results of engine trials with Fischer-Tropsch diesel oils are reported. Compares Fischer-Tropsch and coal-hydrogenation processes and discusses the economics of the former.

1965. KÖRBER, F., AND OELSEN, W. [Thermodynamic Considerations on Some of the Equilibrium Curves in the Iron-Carbon Condition Diagram.] Arch. Eisenhüttenw., vol. 5, 1932, pp. 569-578; Chem. Abs., vol. 26, 1932, p. 5483.

Because of the uncertainty existing, the shape and coordinates of the saturation lines of γ-mixed crystals in α- and β-Fe (GOS) and in cementite (SE) were calculated thermodynamically from the heat-content curves of pure Fe given in the literature. The calculated GOS-line is convex to the concentration axis and the SE-line is straight, in agreement with numerous experimental results. Similar calculations, with the heat of fusion of γ-Fe for the beginning (BC) and the end (JE) of the separation of γ-mixed crystals from the melt, show that in the melt, C is dissolved principally as Fe₃C molecules, and to a smaller extent as C atoms. On the basis of JE- and BC-lines, no definite statement can be made as to the molecular form of C in the γ-mixed crystals. The heat of solution of 1 gm. Fe₃C in γ-mixed crystals is —30.2 cal., the heat of transformation at 781° of 1 gm. of pearlite 20.5 cal., and the heat of formation of cementite —5 to —7 kcal. per mol. Bibliography.

1966. KÖRBER, F., WIEMER. H., AND FISCHER, W. A. [Thermal Disintegration of CO on Fe and Its Alloys and in Mixtures With Carbon.] Arch. Eisenhüttenw., vol. 17, 1943, pp. 43-52; Chem. Abs., vol. 38, 1944, p. 5769.

Catalytic decomposition of pure Fe cause a stronger disintegration of CO at about 900° which, however, if compared with the equilibrium concentrations of Bou-douard's curve, cannot be ascribed to catalytic effects but probably to chemical reactions between the Fe and CO. Admixtures of graphite up to 1.5% do not affect this action of soft-Fe basic bodies. If, however, the basic body contains cementite a very pronounced maximum of CO₂ formation is observed between 500° and 600° at 0.4% C as cementite. This maximum is equal or even higher than the value for soft Fe around 900° depending on the quantity of basic body, and can be observed, though weaker, even at lower cementite contents. Increasing the cementite content increases the maximum value between 500° and 600°, while at 900° it becomes smaller and is hardly noticeable at 1.2-1.5% C. Steel has much less disintegrating action on CO than powdered basic catalytic bodies. Magnetic measurements showed that in passing CO over Fe powder up to 500° the latter is transformed entirely into cementite; the velocity of the transformation depends on the fineness of the Fe powder. Simultaneous formation of higher carbides or any other oxides could not be observed at this temperature.

1967. KOREVAAR. A. [Influence of Water Vapor in Gas Generators.] Chem. Weekblad, vol. 22, 1925, pp. 66-73; Chem. Abs., vol. 19, 1925, p. 1622.

Earlier work is critically reviewed. It is concluded that the water-gas equilibrium H₂O+CO=CO₂+H₂ plays a very unimportant role; it is virtually never reached. The reactions taking place are solely determined by the equilibrium conditions for (I) C+H₂O= CO+H₂ (Lang) and (II) 2CO=C+CO₂ (Boudouard). It is not yet possible to give a complete calculation of the reactions involved. From a technical point of view, Bone and Wheeler's result that only a limited amount of H₂O can be completely utilized, is very important. A partial calculation shows that at a lower temperature of the combustion zone more H₂O vapor can be decomposed.

1968. KORNETZKI, M. [Curie Temperature and Hydrostatic Pressure.] Ztschr. Physik, vol. 124, 1948, pp. 566-569; Chem. Abs., vol. 43, 1949, p. 8783.

Change in Curie temperature with hydrostatic pressure is estimated on the basis of the relation between Curie temperature and the lattice constants for the halides of the metals from V to Cu. The dependence of the Curie temperature of Fe on its lattice constant is an approximate agreement with previous theoretically estimated values.

KORNIICHUK, G. P. *See* abs. 1751.

KORTENGRABER, A. *See* abs. 3059.

1969. KOSTELITZ, O., AND HENSINGER. G. [Catalytic Dissociation and Synthesis of Methanol.] Chim. et ind., vol. 42, 1939, pp. 757-773; Chem. Abs., vol. 34, 1940, p. 3572.

Activities of some ZnO preparations obtained by different processes and treated in various ways were studied in the synthesis of MeOH from CO and H₂, and the catalytic action of these preparations after they had been used for the synthesis were studied on the dissociation of MeOH to see what changes were undergone during the high-pressure synthesis tests. When Merck's pure ZnO₂ is pressed and then decomposed at 300° in an atmosphere of MeOH, the catalytic power per unit vol. of catalyst increases during dissociation of MeOH with the rate of compression; when the ZnCO₃ is first converted to ZnO by heating at 300° in air and is then pressed, the catalytic power per unit vol. of catalyst at first increases with the degree of compression to a maximum at 1,000 atm., and then decreases at higher pressures. If the activity of the preparations is calculated with reference to the values of total dissociation, the following degrees of activity (activity scale) during the dissociation of MeOH are obtained: ZnO pressed under 1,000 atm. has about the same activity as ZnCO₃ pressed under 2,000 atm.; smithsonite (natural ZnCO₃) has a much lower activity. If the numerical values of CO formed by dissociation of MeOH are chosen as a basis for comparison, ZnO pressed under 1,000 atm. is slightly more active than smithsonite, followed by ZnCO₃ pressed under 2,000 atm. The tests on the synthesis of MeOH showed that smithsonite is the most active catalyst, followed in order by ZnO pressed under 1,000 atm. and by ZnCO₃ pressed under 2,000 atm. and subjected to preliminary treatment in an atmosphere of MeOH vapor at 300°. Smithsonite is a good catalyst without having undergone any preliminary treatment, whereas hydrated ZnCO₃ requires special precautions (preliminary treatment in MeOH vapor at 300°). With smithsonite increase in the velocity of circulation of the gases increases the catalytic power per unit vol. of catalyst; with ZnO the reverse is the case. Tests on the dissociation of MeOH with catalysts that had been used for synthesis showed a considerable decrease in the catalytic power, and the specific activity of these catalysts also seemed to have undergone considerable

modifications. ZnO preparations produce chiefly a strong dissociation of MeOH (80–90%) into CO and H₂ and a slight decomposition (10–20%) of the MeOH into secondary products; but, after they had been used for the synthesis of MeOH, they produce little decomposition into CO and H₂ (20–50%), and most of the MeOH is decomposed into secondary products, especially Me formate (15–37% of the initial MeOH). The activity of the catalysts during dissociation of MeOH on the one hand and during synthesis of MeOH on the other is not the same. The study of the catalytic dissociation of MeOH is not a reliable method for determining the most efficient catalysts for the high-pressure synthesis of MeOH. The dissociation reaction seems to be useful merely for furnishing, by means of relatively simple apparatus, a few qualitative data relative to the activity of catalysts for the synthesis of MeOH; to determine the most suitable catalysts it is preferable to carry out synthesis tests under varying conditions of pressure, temperature and quantity of reactants.

1970. KOSTER. W. [Effect of Heat Treatment Below the A₁ Point on the Properties of Technical Iron.] Arch. Eisenhüttenw., vol. 2, 1929, pp. 503–522.

KOTH, A. W. *See* abs. 2576, 2577.

1971. KOTZSCHMAR. —. [Production of Paraffin From Carbon Monoxide and Hydrogen. Experiments to Explain the Unfavorable Outcome of a Large-Scale Experiment at Leuna.] FIAT Reel R–20, frames 7552–7561, Oct. 20, 1939; PB 73,564.

Experiments were carried out in the I. G. Farbenindustrie Ammonia Laboratory, Oppau, in an attempt to explain the failure of a large-scale experiment at Leuna on the production of paraffin from CO and H₂ in the presence of a Co catalyst. After elimination of several possible factors, it was concluded that the conditions of reduction of the catalyst were responsible for the failure of the Leuna experiment. The failure was due to the swift rise in the reduction temperature of the catalyst. Heating for 4 hr. yielded satisfactory catalysts, whereas heating for 15 min. gave poor catalysts.

KOVACS, S. *See* abs. 3374.

1972. KOWALSKI, J., AND GONDZIK, J. [Cracking of Higher-Boiling Benzene Hydrocarbons to Motor Fuel.] Przegląd Górniczy., vol. 6, 1950, pp. 203–208; Chem. Abs., vol. 44, 1950, p. 10307.

Synthetic fraction b. 200°–300° from the Fischer-Tropsch process was cracked at 550° and 5–25 atm. with a contact time of 0.5 sec. to produce 71% of gasoline of 61 octane no. without C formation. Contrary to expectations, a mixture of 71.6% of the synthetic oil and 28.4% of the aromatic fraction from coke-oven-gas manufacture (initial b. p., 156°, 95% up to 193°) will crack at the relatively low optimum temperature of 660° and 25 atm. pressure to yield 65% of gasoline of 78.7 octane no. without any C formation. It is calculated that conversion of the aromatics in the mixture to gasoline was 80% greater than in cracking the aromatic fraction alone. The feasibility of the process on a large scale was confirmed by cracking of mixtures of the synthetic oil and the aromatic fraction in different proportions in a Carburol-type unit of 110-ton-per-day capacity, at a recycle ratio of 5:1.

KOZHENOVA, K. T. *See* abs. 1662.

1973. KOZHINA, N. K. [Behavior of Fe₃C in a Stream of CO₂.] Stal, vol. 1, No. 7/8, 1941, pp. 78–79; Chem. Abs., vol. 38, 1944, p. 3582.

Interaction between Fe₃C and CO₂ was investigated by X-rays. There were 2 series of experiments: In the first powdered pure Fe₃C was heated at various temperatures 200°–800° for 5–60 min. in a stream of pure CO₂; in the 2d the Fe₃C was heated at 400° for 30 min.

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in a stream of CO₂; then the CO₂ was cut off, and the heating continued to 800°–1,200°. In the 1st series, the results were divided into 3 groups: Samples heated at 200°, 300°, and 400° had a predominance of Fe₃C. The predominant phase of samples heated at 500° and 570° was hard to determine. The predominant phase of samples heated at 600°–800° was Fe₃O₄. Lines of FeO appeared on all röntgenograms. In the second series the predominant phase was α-Fe.

KOZLOV, L. I. *See* abs. 1589, 1590.

KRAEBER, L. *See* abs. 2151.

1974. KRAFT, J. [Artificial Motor Fuels.] Bányász. Kohász. Lapok, vol. 70, 1937, pp. 366–370; Chem. Abs., vol. 32, 1938, p. 1425.

General account is given. The method of Fischer-Tropsch is proposed for working up Hungarian coal occurrences in the Mecsek Mountains.

KRÄGELOH, F. *See* abs. 3051.

1975. KRASE, N. W. High-Pressure Gas Research at the University of Illinois. Chem. and Met. Eng., vol. 35, 1928, pp. 463–465; Chem. Abs., vol. 22, 1928, p. 4284.

1976. ———. High-Pressure High-Temperature Technology. Chem. and Met. Eng., vol. 37, 1930, pp. 530–533; Chem. Abs., vol. 24, 1930, p. 5394.

Synthetic NH₃ industry, synthetic MeOH industry, and the hydrogenation of pertoleum industry are the ones using high pressures and temperatures. Flexibility of the hydrogenation process permits refineries to adjust their output in accordance with demands of consuming market, producing gasoline, kerosene, gas oils, or lubricants in the proportions desired. The process permits 100% conversion of crude oils into gasoline of excellent quality, while but 70% is obtained; for example, S as H₂S passes out of the picture. Plants are virtually ready to go into operation to produce higher alcohols from CO and H₂ by pressure-catalytic processes. Fischer's Synthol process and methanation of CO also are high-pressure high-temperature processes of interest to the petroleum industry.

1977. ———. Carbon Monoxide as a Raw Material for Chemical Synthesis. Trans. Am. Inst. Chem. Eng., vol. 32, 1936, pp. 493–510; Chem. and Met. Eng., vol. 43, 1936, pp. 590–595; Chem. Abs., vol. 31, 1937, p. 6763.

Review covering the production, properties, and reactions of CO and its utilization in CO–H₂ mixtures for production of MeOH and higher alcohols and liquid organic compounds.

——— *See* abs. 3195.

KRATZER, M. B. *See* abs. 2341.

1978. KRAUCH, C. [Technical and Economic Considerations on Coal Refining, With Special Reference to High-Pressure Processes.] Stahl u. Eisen, vol. 47, No. 27, 1927, pp. 1118–1126; Jour. Inst. Petrol. Technol., vol. 13, 1927, pp. 347–352A; Erdöl u. Teer, vol. 3, 1927, pp. 455–457; Petrol. Times, vol. 18, 1927, p. 679; Petroleum, vol. 23, 1927, p. 1213; Chem. Abs., vol. 21, 1927, p. 4047.

General discussion.

1979. ———. Catalysis Applied to the Conversion of Hydrocarbons. Proc. Internat. Conf. Bituminous Coal, 2d Conf., 1928, pp. 32–48; Brennstoff-Chem., vol. 10, 1929, p. 9.

General discussion of catalysis with some application to coal hydrogenation and the oxidation of paraffin hydrocarbons to obtain fatty acids. No specific mention of special catalysts.

1980. KRAUT, H., WEISCHER, A., AND HUGEL, R. [Suitability of Fats Synthetized From Fatty Acids of From 6 to 12 C Atoms. I. Preparation of the Synthetic Fats and Their Hydrolysis by Pancreatic

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Lipase.] Biochem. Ztshr., vol. 316, 1943, pp. 96–107; Chem. Abs., vol. 38, 1944, pp. 4626–4627.

Experiments were made with fats from various lower fat acids to determine the lipase action in alkaline or acid medium and in a medium of variable pH. The hydrolysis is greater the smaller the molecular weight of the triglyceride, but no appreciable difference was found between fat acids with even or odd C numbers.

1981. KRAUTWALD, A. [Synthetic Fat as a Foodstuff.] Deut. Gesundheitsw., vol. 3, 1948, pp. 354–356; Chem. Abs., vol. 42, 1948, p. 7898.

Synthetic fat consisted of glycerides of saturated fatty acids, of which 50% had an odd number of C atoms. Analysis showed the following ester composition: Lauric acid 18%, undecanoic acid 18%, tridecanoic acid 20%, myristic acid 8%, palmitic acid 15%, margaric acid 7%, and stearic, nonadecanoic, arachidic, and capric acids totaled 3%. The remaining 11% were high boiling point esters. Synthetic fat looked like butterfat, was solid at room temperature and was virtually without taste or odor. Its melting point was 36.5°, saponification no. 235, I no. 11. It could be stored for 2 years without apparent change in taste or odor. Persons in good health were able to digest 100 gm./day. It was well tolerated even by patients with liver or stomach ailments in amounts up to 50 gm./day. It was absorbed from the intestines and easily metabolized. Ingestion of a 50-gm. dose produced a fall in respiratory quotient in a mannere similar to butter. Experimentally induced ketosis in healthy persons could be reduced by administration of synthetic fat.

1982. KRENS. R. W. Development of Synthetic Fuels From Natural Gas. Petrol. Refiner. vol. 26, No. 10, 1947, p. 171.

Paper at the Southwest Louisiana Sec. meeting, American Chemical Society, discusses the reserves of liquid fuel that can be made available from our resources of natural gas, coal, and oil shale at varying gasoline price levels, and presents simplified diagrams of some of the process equipment that will be utilized.

1983. KREULEN, D. J. W. [Physical and Chemical Constants of Two Completely Hydrogenated Oils Prepared by the Fischer-Tropsch Gasoline Synthesis.] Chem. Weekblad. vol. 35, 1938, pp. 410–411; Chem. Abs., vol. 32, 1938, pp. 7252.

These lubricating oils differ markedly from natural petroleum products in that the aliphatic side chains are very much branched. The molecular weights (774 and 457, d. 0.8580 and 0.8453) are different, but the molecular constitutions are parallel; in both cases the viscosity poleheights are identical, although the viscosity time indexes are different. The Ubbelohde law that oils of the same origin have the same pole height is confirmed.

1984. ———. [The Chemism of the Fischer-Tropsch Synthesis.] Chem. en Pharm. Tech., vol. 3, No. 12, 1948, pp. 205–206; Chim. et ind., vol. 61, No. 2, 1949, p. 151.

Standard catalyst for this synthesis is composed of Co : Th : Mg : kieselguhr in the proportion of 100 : 5 : 8 : 200. The Th may be omitted and the quantity of Mg decreased. The kieselguhr has a double role; it insures a very fine division of the Co and renders the catalyst porous. It is very improbable that Co carbide is formed as an intermediate product. The mechanism of the polymerization reaction has not yet been clarified.

1985. KRICHEVSKII, I. R., AND KHAZANOVA, N. E. [The ε-Phase of Iron Nitride.] Doklady Akad. Nauk S. S. S. R., vol. 71, 1950, pp. 677–680; Chem. Abs., vol. 45, 1951, p. 1410.

Equilibrium constant K_1 of the reaction $[2n/(n-m)]$ $Fe_mN = [2m/(n-m)] Fe_nN + N_2$ where Fe_mN is the ε-

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phase and Fe_nN is the γ-phase, was calculated from existing data for the synthesis of NH₃ and for the reaction of Fe nitrides with H₂. The values obtained for log K_1 were: 400° 5.616, 450° 5.555, 500° 5.491, 550° 5.433, and 600° 5.382. By combining these values with data on the fugacity of N₂, the N₂ pressure in equilibrium with the ε- and γ-phases at 400°–600° was calculated at approximately 12,000–13,600 atm.

1986. ———. [Nitriding of Iron.] Doklady Akad. Nauk. S. S. S. R., vol. 71, 1950, pp. 481–484; Chem. Abs., vol. 44, 1950, p. 10,631.

Specimens of Fe were nitrided at 375°, 400°, 450°, and 500° at atmospheric pressure in NH₃–H₂ mixtures, the NH₃ content ranging 35–65%. The nitriding reaction stopped almost completely as a limiting N₂ content in the Fe was approached, the final N₂ content increasing with increase in temperature or NH₃ concentration. Nitriding is the result of 2 opposing reactions: (1) $2 NH_3 + 2xFe \rightarrow 2 Fe_xN + 3 H_2$, and (2) $2 Fe_xN \rightarrow 2xFe + N_2$. Reaction (1) is limited by rate of diffusion of N₂ through Fe and Fe nitrides, and because of the low rate of diffusion through Fe nitrides, the reaction slows down as the nitrides increase until equilibrium between the 2 reactions is attained.

KRIEG. A. *See* abs. 43a, 44, 46, 48, 49.

1987. KRIEG. A., DUPASH, A. P., AND ANDERSON. R. B. Improved Caustic Scrubber. Ind. Eng. Chem., vol. 41, No. 7, 1949, p. 1508.

Description of small laboratory scrubber for removing CO₂ from the exit gas of the Fischer-Tropsch synthesis.

1988. KRINGS, W., AND KEMPKENS, J. [Solubility of Oxygen in Solid Iron. I.] Ztschr. anorg. Chem., vol. 183, 1929, pp. 225–250; Chem. Abs., vol. 24, 1930, p. 44.

Fe used was prepared by reduction of pure Fe₂O₃ in dry H₂ at 720°–750°. The solubility of O₂ in this Fe was determined by means of equilibrium experiments in a current of H₂–H₂O vapor at 715° and was found to be 0.11±0.015%. The same experiments served for a study of the equilibrium $FeO + H_2 \rightleftharpoons Fe + H_2O$.

1989. ———. [Solubility of Oxygen in Solid Iron. II.] Ztschr. anorg. Chem., vol. 190, 1930, pp. 313–320; Chem. Abs., vol. 24, 1930, p. 3974.

By measurement of the O₂ pressure of Fe–O mixed crystals with H₂O–H₂ mixtures, the solubility of O₂ in solid Fe at 800° was found to be 0.095±0.01%. At 715° the value of 0.11±0.015% had been previously determined. These results were confirmed by the decomposition of freshly prepared Fe₂O₃ in the same gas mixture.

1990. KROEPELIN, H. [Heat Transfer in the Fischer-Tropsch Synthesis, Especially in Lamella Furnaces.] Erdöl u. Kohle, vol. 3, No. 1, 1950, p. 10.

Paper presented at the 1949 meeting of the Deutsche Gesellschaft Mineralölwissenschaft u. Kohlechemie. The transfer of the reaction heat set free in the Fischer-Tropsch synthesis is traced from the middle of the catalyst bed to the H₂O space of the catalyst furnace. The problem is divided into 4 parts: (a) From the middle of the catalyst bed to the lamella, (b) from the lamella to the cooling space, (c) from the tube wall to the cooling H₂O, (d) from the path of the steam in the cooling tube to the steam accumulator. The heat transfer within the catalyst bed as in the lamella is calculated by the same formula, which shows a quadratic dependence between temperature and path. For the main reaction zone, in which 86,000 kcal. per hr. are generated in 1 m.³ of catalyst, the following temperature differences are shown: (a) In the catalyst bed about 8°; (b) in the lamella, 3°; (c) in the water-tube wall, 1°. Experimental and operating tem-

perature measurements are presented for an active catalyst. Measurements of H_2O circulation in a synthesis furnace as well as its calculation is given briefly.

1991. KROEPELIN, H., OPITZ, W., AND FREISS, W. [Sulfochlorination of Kogasin in the Dark.] Erdöl u. Kohle, vol. 2, 1949, pp. 498–500; Fuel Abs., vol. 7, 1950, pp. 3133.

Tests on the reaction of Kogasin (b. 225°–305°) with Cl_2 and SO_2 were made using Kogasin of 3 grades of purity, technical, refined (olefin-free), and a super-refined material (olefin-free vacuum-distilled over Na in N_2). Using the refined material, chlorination was the main reaction at 25°–38° and sulfochlorination at 38°–68° (temperature measured in reaction vessel). The best ratio between chlorination and sulfochlorination was at 68°. Technical Kogasin reacted similarly but somewhat more energetically. Using the highly refined Kogasin, reaction with $Cl_2 + SO_2$ could not be obtained. In the course of analyses of the Kogasins, marked sensitivity of the refined olefin-free material to O_2 was observed in the temperature range 100°–130°. Tests with the most highly refined material to which 0.5% of chain initiators (dodecylene-1, benzoyl peroxide) had been added showed strong combination with Cl_2 and SO_2 at 71°–77°, the products containing approximately 16% Cl and 9% S. Inhibitors of the reaction (alcohols, pyridine) also were tested. In the case of pyridine the inhibitory action is due to a pyridine-chlorine compound. Smooth sulfochlorination of petroleum fractions from crude oil was not obtained, presumably owing to the presence of natural inhibitors. The experiments confirm that, even in the dark, sulfochlorination is a chain reaction.

1992. KRÖGER, C. [Action of Inorganic Polycatalysts in the Water-Gas Process.] Ztschr. Elektrochem., vol. 44, 1938, pp. 577–578; Chem. Abs., vol. 32, 1938, p. 9446.

Oxides of Cu, Ni, Co, Fe, U, and Mn, or alkali carbonates promote the water-gas reaction when mixed with coke, graphite, lampblack, or wood charcoal. The catalytic activity of K_2CO_3 is promoted by CuO, Co_3O_4, Ag_2O, or ZnO when added to graphite. Low-temperature coke or wood charcoal is activated by Li_2CO_3. The addition of K_2CO_3–Co_3O_4 or K_2CO^3–CuO to lignite coke or wood charcoal gives a lower yield than when these substances are added to graphite. The action of the catalysts depends upon the fixation of the free alkali metal on the surface of the C and its infiltration into the graphite lattice. When steam reacts the lattice is destroyed.

———. *See abs. 2436.*

1993. KRÖGER, C., AND MELHORN, G. [Action of Inorganic Additions as Single and Multiple Catalysts in the Water-Gas Reaction.] Brennstoff-Chem., vol. 19, 1938, pp. 157–169; Chem. Abs., vol. 32, 1938, p. 8744.

In apparatus and procedure previously described the action of various metal oxides on the gasification of graphite with steam at 600°–800° has been studied. Oxides with medium heats of formation were found most active. None, however, surpassed CuO, which gave 22% steam decomposition at 700°, graphite alone, only 6%. Next, in order of decreasing activity, were oxides of Cr, Ni, Fe, U, Tl, Mn, Co, and Al. Combinations of these did not increase effects. With alkaline carbonates, the order was K and Na, 32% decomposition at 660°, Rb, Cs, and least, Li. Greatest steam decompositions, 65% at 650°, were obtained with K_2CO_3 combined with CuO and Co_3O_4; these and NiO also gave results above the additive expectations. A ternary K–Ni–Co mixture gave results similar to K_2CO_3. The electronegative position of K is offered in explanation of its superior effect in reaction mechanisms offered. Formation of unsaturated hydrocarbons was

observed in the reaction when additions of Hg, Te, Th, and U oxides, Li_2CO_3, and mixtures with K_2CO_3, were made to the graphite, ThO_2 producing 2.1% at 711°. Composition of the reaction gas showed that equilibrium is established beginning at 570° with activated graphite. No establishment of the Boudouard equilibrium was found. The literature is reviewed briefly, with 72 ref.

KRONIG, W. *See abs. 3459.*

1994. KRONSTEN, J. A. Poland's Oil Position Today. Synthetic and Substitute Products. Petrol. Times, vol. 51, 1947, pp. 159–160.

Of the 3 German-built synthetic plants on Polish territory, not one is in a fit condition to be rebuilt. They will, therefore, be combined at the site of the Oswiecim synthetic oil works, which will be equipped with plant allocated to Poland under the German reparation scheme and coming from the Fischer-Tropsch plant at Schwarzheide near Dresden. Also, a certain amount of salvaged equipment will be transferred from the works at Blachownia-Blechhammer, formerly the Schlesische Hydrierwerke A.-G. and from Kedzierzyn in Silesia. The new works at Oswiecim will have an output of 40,000 tons per yr. of intermediates for further processing into motor fuel and other products, but plant completion is unlikely before 18–24 months.

1995. KROUPA, G. [Profitableness of Obtaining Oil From Water Gas.] Petrol. Ztschr., vol. 23, 1927, pp. 1524–1525; Chem. Abs., vol. 22, 1928, p. 1464.

Synthetic production of oil from water gas is uneconomical at the present time as compared with the hydrogenation of coal, and even though the process proves to produce the greatest yield of products, the cost of production will remain prohibitive. The water-gas process is slow and uneconomical because of the several additional steps that must be introduced including distillation, gasification, chemical gas purification, and the synthetic operation.

KRSEK, G. *See abs. 3, 4.*

1996. KRUG, J. A. Report of the Secretary of the Interior on the Synthetic Liquid Fuels Act. 1946. 1947, 82 pp.

Report covers the work of the Bureau of Mines for 1946. It is divided into 2 parts; the 1st summarizing the major progress and developments of the year, and the 2d giving a detailed account of the engineering and scientific achievements. As the result of the research in the field of synthetic fuels, it is concluded that gasoline may be produced from coal or oil shale at a cost of $0.075–$0.095 per gal., and from natural gas at $0.055–$0.07 per gal., exclusive of any profit or interest on the investment. Construction is far advanced at 2 of the major Bureau projects for the small-scale investigation of coal hydrogenation by the Bergius process and the production of synthetic gasoline by the Fischer-Tropsch reaction. Furthermore the oil-shale demonstration plant in Colorado is expected to start operation soon. In this project fundamental data on the design of oil-shale and pilot-plant units have been worked out. A thermal-solution process is being developed for shale oil recovery, which shows more oil obtained than the shale assay has indicated. Two shale mines will supply the demonstration plant with shale and will determine commercial mining costs; these are expected to be about $0.50 per ton of shale. Underground gasification of coal is undergoing experimental tests in Alabama to determine the possibilities for the production of synthesis gas. A coal liquefaction plant is being prepared at Louisiana, Mo. from a Government-owned NH_3 plant to produce up to 200 bbl. of oil per day. Laboratory studies are being made at Morgantown, W. Va. to develop cheaper and better methods for producing CO and H_2 for synthesis gas

and for coal hydrogenation. Lower pressures, lighter equipment, minimum H_2 consumption, and the use of dry coal without a vehicle or with one readily flashed off are indicated in the coal-hydrogenation process as contributing greatly to the reduction of production costs, while in the synthesis process production rates 3–5 times those of German plants have been indicated through use of a new type of internally cooled converter embodying an improved cooling method consisting in dripping a cooling oil directly over the catalyst preferably in cocurrent flow at high space-velocities of the synthesis gas. Besides the increased production reported, there are the further advantages of a lower content of gaseous hydrocarbons in the product, the possibility of greatly enlarged reaction chambers, and the use of a wider range of catalysts in comparison with fluidized types. Still other methods of cooling are under investigation such as liquid-phase suspended catalyst and hot-gas recycle.

1997. ———. Report of the Secretary of the Interior on the Synthetic Liquid Fuels Act from January 1, 1947, to December 31, 1948, 128 pp. Combustion, vol. 19, February 1948, pp. 49–51; Petrol. Processing, vol. 3, 1948, pp. 207–208; Chem. and Eng. News, vol. 26, 1948, pp. 610–611.

Progress made in the development of industrial methods for the production of synthetic liquid fuels is reported. Projects under way include both demonstration plants and laboratory and pilot-plant investigations of shale oil, coal hydrogenation, synthesis gas by complete gasification of coal in presence of O_2 and steam, the Fischer-Tropsch process, and subterranean gasification of coal. In addition, experimental work is being carried on in connection with the production of liquid fuels from agricultural wastes. Operations in oil shale are concerned with both mining and processing. The use of large-scale equipment in the mining of shale has reduced the mining cost to $0.70 per ton and it is expected to reduce this to $0.50 per ton. The best figure obtained thus far in preparing the shale for retorting is $0.16 per ton and for retorting $0.096 per gal. of liquid crude shale oil. It is believed the ultimate figure will be $0.05 per gal. A coal hydrogenation plant with a capacity of 250 bbl. gasoline per day will be completed in 1948. Economic studies have shown that by using coke-oven gas as the source of process gas, fuel oil can be made for approximately $0.07–$0.11 per gal. The cost of high-pressure H_2 is approximately 40–50% of the total cost of producing fuel oil. Dry hydrogenation is being investigated as indicating a lower content of asphaltic material in the product. Two types of coal solvents also are being investigated toward development of a liquefaction process operating at moderate temperatures and low H_2 pressure. One type, such as o-cyclohexyl-phenol, effects chemical dissociation and H_2 transfer to the coal molecule; and the other, such as phenanthrene, acts as a dispersing agent for the coal. Initial tests are being made on the gasification of powdered coal with O_2 and steam in a reactor of the vortex type with a capacity of approximately 100 lb. of coal per hr. A complete Fischer-Tropsch synthesis plant of about 80-bbl.-per-day capacity is being designed to provide engineering and cost information. The plant will be erected at Louisiana, Mo. Research is being continued on the liquid-phase catalyst suspension process as well as internal oil cooling of the catalyst. Encouraging results are being obtained in the gasification of pulverized coal entrained in superheated steam and O_2, and promise is made of considerable cost reductions for synthesis gas under that achieved in standard water-gas sets. The favorable results obtained with underground coal-gasification tests warrants further study and investigation will be continued. The cost of the Gorgas, Ala., project is reported as

$2.33 per ton of coal gasified, and a gas is obtained of calorific value 125 B. t. u. per cu. ft.

1998. ———. Synthetic Liquid Fuels. 1948 Annual Report of the Secretary of the Interior. I. Oil From Coal. II. Oil From Oil Shale. III. Liquid Fuels From Agricultural Residues. IV. Secondary Recovery and Petroleum Chemistry and Refining Research. Bureau of Mines Repts. of Investigations 4456, pp. xviii, 1–62; 4457, pp. xviii, 1–57; 4458, pp. xviii, 1–25, January 1949.

Comprehensive review of all of the phases of the Government's synthetic liquid fuels development program. Detailed engineering studies and cost estimates of the various processes.

KRYUKOV, Y. B. *See abs. 152, 152a.*

1999. KUBELKA, P., AND WENZEL, W. [Equilibrium Relations Involved in the Interaction of Water Vapor and Methane. I.] Metallbörse, vol. 21, 1931, pp. 1227–1228; Brennstoff-Chem., vol. 12, 1931, p. 380; Chem. Abs., vol. 25, 1931, p. 5612.

Develops equilibrium constants for all the steps and for the complete reaction of H_2O vapor and CH_4 for the production of H_2 under isobaric conditions. Mathematical expressions for evaluating the partial pressure of each of the gases, CH_4, CO_2, and CO, in terms of equilibrium constants and the partial pressure of the other components.

2000. ———. [Equilibrium Relations Involved in the Interaction of Water Vapor and Methane. II.] Metallbörse, vol. 21, 1931, pp. 1275–1276; Brennstoff-Chem., vol. 12, 1931, p. 380; Chem. Abs., vol. 25, 1931, p. 5612.

Mathematical expressions are modified to give actual weight and vol. % ratios, and tables are compiled for temperatures 550°, 650°, 750°, 850°, and 1,000° or above (1,200°) showing the effect of varying the H_2O vapor 0.5–4 mol. per mol. CH_4, both with and without H_2 introduced with the CH_4.

2001. ———. [Equilibrium Relations Involved in the Interaction of Water Vapor and Methane. III.] Metallbörse, vol. 21, 1931, pp. 1372–1373; Brennstoff-Chem., vol. 12, 1931, p. 380; Chem. Abs., vol. 25, 1931, p. 5612.

Further tables showing equilibrium relations at the temperatures shown in pt. II (*see abs. 2000*).

2002. ———. [Equilibrium Relations Involved in the Interaction of Water Vapor and Methane. IV.] Metallbörse, vol. 21, 1931, pp. 1421–1422; Brennstoff-Chem., vol. 12, 1931, p. 380; Chem. Abs., vol. 25, 1931, p. 5612.

Above 850° from a general consideration of tables and graphs it was shown that (1) when excess water vapor is avoided the reaction is virtually according to the equation of $CH_4 + H_2O \rightarrow CO + 3\ H_2$; (2) with an excess of water vapor at intermediate temperatures around 750° the CH_4 is most effectively decomposed for the production of H_2 virtually according to the equation $CH_4 + 2H_2O = CO_2 + 4H_2$.

2003. KUNOKAWA, M. Activated Adsorption of Methane on Reduced Nickel. Proc. Imper. Acad. (Tokyo), vol. 14, 1938, pp. 61–66; Rev. Phys. Chem. Japan, vol. 12, 1938, pp. 157–167; Chem. Abs., vol. 32, 1938, p. 5678.

Adsorption of CH_4 on Ni was studied at pressures 5–10^{-3} mm. Between $-112°$ and $20°$ adsorption is due to van der Waals' forces. The heat of adsorption is 1 kg.-cal. per mol. Above 40°, activated adsorption takes place. Isotherms were obtained up to 250°. The mechanism is assumed to be: $CH_4 \rightarrow CH_2 + H \rightarrow CH_2 + 2H \rightarrow CH + 3H \rightarrow C + 4H$. The desorption process consists in the formation of CH_4 by the hydrogenation of CH radicals. The heat of activated adsorption of CH_4 on

Ni is calculated to be 12 kg.-cal. per mol. if the difference between the 0-point energy of the CH and the CD bond is taken as O.

2004. ———. [Decomposition of Methane on Reduced Nickel.] Rev. Phys. Chem. Japan, vol. 12, 1938, pp. 90–104; Chem. Abs., vol. 33, 1939, p. 1579.

Equilibrium constant and the reaction velocity of the catalytic decomposition of CH_4 on reduced Ni were measured in the temperature range 420°–500° below 30 mm. pressure. The reaction velocity in the initial stage is given by: $dx/dt = k(a-x)/x^n$, where a is the initial amount of CH_4, x the decomposed amount at time t, k, and n constants. The retardation exponent, n, was always larger than unity when the catalyst was activated by reduction with H_2, and it became smaller than 1 when the catalyst was used repeatedly without being reduced and also when temperature was lowered. No effect of added H_2 was observed. These results agree with those for Pt catalyst.

2005. KUCHINKA, R. [Synthesis of Edible Fats From Coal by Fischer-Tropsch Products and Air by Paraffin Oxidation.] Pharmazie, vol. 3, 1948, pp. 439–444; Chem. Abs., vol. 43, 1949, p. 5878.

Survey of methods of synthesis, especially of the higher fatty acids and technical processes developed. Points out need for further study of the physiological action of the synthetic fats, especially of the nonsaponifiable fractions.

——. See abs. 2566.

KÜHN, J. See abs. 425.

KUMMER, J. T. See abs. 831, 831a, 2718.

2006. KUMMER, J. T., AND EMMETT, P. H. Chemisorption of Carbon Monoxide and the Heterogeneity of the Surface of Iron Catalysts. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 2886–2889.

Radioactive and nonradioactive samples of CO have been added in succession as two separate fractions to a reduced Fe synthetic NH_3 catalyst at −195° or −78°. The chemisorbed CO layer has then been removed by pumping and analyzed for $C^{14}O$. The results show that the 2d fraction of added CO tends to desorb first. However, the results also show that a partial rapid exchange equivalent to a coverage of about 50% of the Fe surface occurs between the 2 added fractions of chemisorbed CO even if both fractions are added at −195°.

2007. ———. Study of the Amount of Hydrogen Left on the Surface of a Reduced and Evacuated Iron Synthetic Ammonia Catalyst. Jour. Phys. and Colloid Chem., vol. 55, 1951, pp. 337–345.

To remove one of the uncertainties in measuring the adsorption of H_2 on metal catalysts, it is necessary to determine the amount of H on the catalyst at the start of the adsorption run. To determine the amount of residual H present on samples of pure and of promoted iron synthetic ammonia catalysts use was made of H isotopes after the catalysts had been degassed for a number of hours at 500°. The procedure is described. It was found that promoted iron synthetic ammonia catalysts, but not pure iron catalysts, retain enough H after 24-hr. evacuation at high temperature (about 500°) to be equivalent to the covering of 5–35% of the metallic surface, or 1–10% of the part of the surface covered with promoter. Accordingly, due account should be taken of this residual H in any adsorption measurements on promoted iron catalysts.

2008. KUMMER, J. T., BROWNING, L. C., AND EMMETT, P. H. Thermodynamic Calculations Concerning the Possible Participation of the Carbides of Iron as Intermediate in Fischer-Tropsch Synthesis. Jour. Chem. Phys., vol. 16, No. 7, 1948, pp. 739–740; Chem. Abs., vol. 42, 1948, p. 6623.

It is concluded from thermodynamic considerations that neither n-mono-olefins nor the higher n-paraffins can be formed from CO and H_2 by reduction of the bulk or the hexagonal Fe_2C or Fe_2C by H_2. It is indicated, however, that the lower normal paraffins with n as high as 6 could, as far as thermodynamic limitations are concerned, be formed under Fischer-Tropsch synthesis conditions by reduction of bulk Fe_2C by H_2.

2009. KUMMER, J. T., DEWITT, T. W., AND EMMETT, P. H. Some Mechanism Studies on the Fischer-Tropsch Synthesis Using C^{14}. Jour. Am. Chem. Soc., vol. 70, 1948, pp. 3632–3643; Chem. Abs., vol 43, 1949, p. 2081.

Fischer-Tropsch synthesis experiments using C^{14} as a tracer show that the greater part of the product of synthesis is formed by some process other than by the reduction of carbide as an intermediate. Only about 10% of the hydrocarbon product appears to have been formed through the carbide for Fe catalysts at or below 260° and for Co at 200°; at 300° the part of the reaction occurring through the carbide reduction mechanism seems to average about 16%. The % formed through the adsorbed phase is not critically dependent on the H_2:CO ratio in the range 1:1–3:1, on the total pressure of the synthesis, within the limits 150–800 mm. pressure; or on the % Fe_2C initially present in the range +100%. The exchange of the C in the gases, CH_4, CH_4H_{16}, butene–1, and C_4H_6, with an Fe carbide surface at 250° is found to be very low; CO exchange with the C in the carbide is only about 5% in 30 min. at 250°, but is as high as 29% in 7 min. at 322°. The mechanism of carbiding has been investigated and has been shown to be complicated by the possibility of a nonuniformly reacting surface. No completely satisfactory picture of the mechanism of carbiding has been formulated.

2010. KUMMER, J. T., PODGURSKI, H. H., SPENCER, W. B., AND EMMETT, P. H. Mechanism Studies of the Fischer-Tropsch Synthesis. Addition of Radioactive Alcohol. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 564–569; Chem. Abs., vol. 45, 1951, p. 4907.

To help elucidate the mechanism of Fischer-Tropsch synthesis, methyl-labeled and methylene-labeled radioactive EtOH were added to a 1:1=CO:H_2 synthesis gas passed at 1 atm. pressure over an Fe catalyst at about 230°. Measurement of the radioactivity of the hydrocarbon products shows negligibly small activity for all CH_4 formed and an approximately constant activity of 2,150±100 counts per minute per cc. S. T. P. for the C_2–C_{10} hydrocarbons. The C_2, and C_4 hydrocarbons have activities of about 1,825. 1,850, and 2,000 counts per minute per cc. Degradation experiments on the C_3 hydrocarbons show that about 90% of the added C atoms are attached to the α–C atom of the alcohol adsorption complex, whereas 10% are attached to the β–C. These results suggest that either EtOH or some surface complex formed by the adsorption of EtOH behaves like an intermediate in hydrocarbon synthesis over Fe Fischer-Tropsch catalysts and that at least the 1st of the added C atoms attaches itself principally to the α–C atom of the surface complex.

KUNG, K. M. See abs. 1508.

KURAKU, H. See abs. 1959a.

2011. KURDYUMOV, G. [X-Ray Investigation of the Structure of Tempered Carbon Steel.] Ztschr. Physik, vol. 55, 1929, pp. 187–198; Chem. Abs., vol. 23, 1929, p. 4658.

Steel sample containing 1.44% C was studied by the Debye-Scherrer powder method. The changes in property of hardened steel on annealing in the temperature range of 100°–150° depend upon the destruction of the tetragonal form, which tends to go into the cubical lattice. The 2d change is due to the decomposition of austenite and the 3d change is connected with the formation of the mixture of α-Fe and

cementite. These 3 changes have been found previously by a study of thermal expansion and electrical conductivity by G. Kurdjumov, and E. Kaminskii.

———. See abs. 70.

2012. KURDYUMOV, G., AND LYSSAK, L. Application of Single Crystals to the Study of Tempered Martensite. Jour. Iron Steel Inst. (London), vol. 156, 1947, pp. 29–36; Chem. Abs., vol. 42, 1948, p. 82.

Martensite tempered at 125–150 hr. has a tetragonal lattice with an axial ratio of about 1.012 and represents the partly decomposed solid solution of the C in α-Fe. After tempering at 150° a certain amount of C, 0.3–0.5%, remains in solid solution and decreases as the tempering temperature rises until after tempering at temperatures above 300° less than 0.1% C remains in solution. 15 refs.

2013. KURDYUMOV, G., AND SACHS, G. [Mechanism of Steel Hardening.] Naturwissenschaften, vol. 18, 1930, p. 534; Chem. Abs., vol. 24, 1930, p. 4746.

Mixture of austenite and martensite crystals from slow solidification and subsequent chilling of a 1.5% C steel was studied for crystal nature and orientation. The (011) plane of the tetragonal crystallites always was parallel to the (111) planes of austenite, also (111) direction to (101), giving an 8° angle between tetragonal axis and austenite axis. This position repeats itself 24-fold in agreement with general cubical symmetry. It can be derived from a superposition of 2 simple slip motions.

2014. ———. [The Mechanism of Hardening Steel.] Ztschr. Physik, vol. 64, 1930, pp. 325–343; Chem. Abs., vol. 25, 1931, p. 271.

Austenite, γ-iron, chilled from 1,100° to room temperature is partly converted into a tetragonal modification, as shown by X-ray diagrams, Debye-Scherrer, from a rotating rod of the material. The dark ground of the films points to considerable irregularities in the arrangement of the atoms of the crystal lattice. Tempering leads to formation of martensite. The lattice distortion (continuous ground) diminishes with increasing temperature and time of tempering. The relative orientation of the crystals of the austenite modification, the tetragonal phase and the γ-iron has been found and the possible course of the rearrangement is discussed.

2015. KURIN, N. P. [Investigations of the Activities of the ZnS–CuS Methanol Catalysts.] Nauch. Tekh. Konferentsiya v Svyazi s Sorokaletnim Yubileem Uchebno-Nauch. Deyatel-nosti Tomsk. Ind. Inst., Tezisy Dokladov, 1940. pp. 108–110; Khim. Referat. Zuhr., vol. 4, No. 4, 1941, p. 100; Chem. Abs., vol. 37, 1943, p. 5306.

ZnS–CuS catalysts were obtained by the separate precipitation of ZnS and CuS, and they contained various amounts of CuS. Pure CuS and ZnS also were studied. The activities of the catalysts were determined by the decomposition of MeOH vapors at volume velocities 420–2,100 (vol. of vapor/unit vol. of catalyst/unit vol. of catalyst/hr.) and at temperatures 250°–450°. Data for catalysts possessing a maximum activity are given. H_2S poisoned the catalysts, but their activities were restored by the passage of MeOH vapors. The decomposition velocity constants of MeOH were calculated. The relation between log k and $1/T$ indicated that the decomposition process of MeOH took place through two stages. The 1st stage presumably was the decomposition of MeOH into HCHO and H_2 and the second stage the decomposition of HCHO into CO and H_2. The activation energies of these reactions were determined.

2016. ———. [Investigation of the Activity of Ammonia Catalysts Reduced by Pure Hydrogen.]

Nauch.-Tekh. Konferentsiya v Svyazi s Sorokaletnim Yubileem Uchebno-Nauch. Deyatel-nosti Tomsk. Ind. Inst., Tezisy Dokladov, 1940, pp. 112–113; Kim. Referat. Zhur., vol. 4, No. 4, 1941, p. 88; Chem. Abs., vol. 37, 1943, p. 5560.

Remelted NH_3 catalyst containing Fe_3O_4, Al_2O_3, and K_2O was used for investigating the reduction process and the activity of the catalyst by the dynamic method at atmospheric pressures, at various temperatures, and various volume velocities. At constant volume velocities, the reduction velocity of the catalyst by H_2 increased with the increase in temperature. The use of H_2 for the reduction (instead of the H_2+N_2 mixture) increased the activity of the catalyst. The optimum conditions for the reduction were obtained at large volume velocities and at temperatures equal to approximately 450°.

KURODA, R. See abs. 1870, 1871.

2017. KUROKAWA, M., AND TAKENAKA, Y. [Thermal Effect on the Catalyst of the Water–Gas Reaction.] Jour. Soc. Chem. Ind. (Japan), vol. 40, 1937, B, p. 347; Chem. Abs., vol. 32, 1938, p. 1354.

Fe_2O_3 catalyst generally used for the conversion of CO and H_2O to H_2 and CO_2 is impaired by the heat of the exothermic reaction. The conversion at 450° was measured with promoted Fe_2O_3 catalysts before and after heating to 850°. The resistance of the catalyst to heat was greatly improved by additions of Cr_2O_3 and MgO. The optimum ratio Fe_2O_3 : Cr_2O_3 : MgO was 1 : 0.1 : 0.03. The catalyst obtained by precipitation with KOH was better than that with NH_3.

2018. ———. Hydrogen by Water–Gas Reaction. Repts. Imperial Fuel Research Inst. Japan, No. 41, 1939; Jour. Fuel Soc. Japan, vol. 19, 1940, pp. a21–26; Fuel, vol. 19, 1940, pp. 146–149; Chem. Abs., vol. 34, 1940. p. 5603.

Activity of the catalyst under standard testing conditions and the effect of temperature and S compounds on the activity of the catalyst are shown. The results with a semicommercial plant are given. It is concluded that the Fe_2O_3+10% Cr_2O_3+3% MgO catalyst can be efficiently used in the practical application of the water-gas reaction for the manufacture of H_2.

2018a. KUROSAWA. K. Pulverized–Coal Gas Producer. Jour. Fuel Soc. Japan, vol. 30, 1951, pp. 7–13; Chem. Abs., vol. 46, 1952, p. 3,237.

Problems relating to this subject are analyzed from the standpoint of low-grade domestic coal. When compared with the Winkler producer, the plant for gasification of pulverized coal for synthesis gas has the advantage that any kind of coal can be gasified, the capacity is large, the construction is simple, the elasticity of capacity is good, and the danger of clinker formation is small. Fine coal used in the plant contained 75% of powders under 4.900 mesh. The rate of gasification is 155–200 kg. per m^3 per hr. The utility of C is 95%. The gasification chamber must be constructed almost spherically for efficient use of radiating heat. As the temperature in the chamber is very high, special attention must be paid to the selection of firebrick and to heat recovery, but the higher construction expenses can be sufficiently compensated by the greater rate of gasification. The minimum economic unit of this plant is about 10,000 m^3 per hr. According to the heat balance, the synthetic heat efficiency is 78% when the sensible heat of gas produced is recovered by the waste heat boiler. The necessary equipment for a 10,000 m^3 per hr. plant is briefly described, and the construction costs and gas production cost are estimated; the possibility of cheap synthesis-gas production with log-grade domestic coals is suggested.

KURZEN, F. See abs. 3067, 3069.

2019. KUSAMA, T., AND YUKIO, U. Thermal Decomposition of Methane. Bull. Inst. Phys. Chem. Research, vol. 8, 1929, pp. 1–11; abs., vol. 2, p. 1; Chem. Abs., vol. 23, 1929, p. 1866.

CH₄ has been pyrolyzed on several catalysts: (a) Pure Ni. (b) Ni+kieselguhr, (c) same as (b) but deprived of its activity by being used to reduce C₁₀H₈, and (d) reduced Fe: (b) and (c) are equally suitable. X-ray spectrograms show that C thus obtained is graphite, which was also proved by the graphitic acid method. This graphite has catalytic properties, which are due to the presence of small amounts of Ni from the catalyzer. By determining the S content of the catalyzer before and after a run, it was ascertained that natural gas contains a certain quantity of S but only a negligible amount. HCl is better than HNO₃ to recover the catalyst, and a new catalyzer produced by the reduction of NiCl₂ is as active as one obtained from Ni(NO₃)₂. H₂ obtained by the pyrolysis of CH₄ always contained some CH₄ that could not be removed, but the mixture can be used very satisfactorily to reduce C₁₀H₈.

2020. KUSS. E. [Decomposition Mechanism of Methanol.] Angew. Chem., vol. 49, 1936, pp. 483–486; Chem. Abs., vol. 30, 1936, p. 6321.

Experiments were carried out in a modified Stock apparatus, which is described. The reaction products were: CH₂O, Me₂O, H₂, H₂O, CH₄, CO, CO₂, and C. The quantitative findings could be expressed by the following equations:

(1) $MeOH \rightleftharpoons CH_2O + H_2$
(2) $2MeOH \rightleftharpoons Me_2O + H_2O$ } Primary
(3a) $Me_2O \rightleftharpoons CH_4 + CH_2O$
(3b) $Me_2O \rightleftharpoons CO + C + 3H_2$
(4) $CH_2O \rightleftharpoons CO + H_2$
(5) $2CO \rightleftharpoons CO_2 + C$
(6) the CH₄ equilibrium

With quartz glass, in opaque pieces, the decomposition did not begin below about 600°, and quartz tubes were therefore used as contact tubes in further experiments. With Ag, as Ag wool (analysis: 0.0544% Cu, traces of Pb, and 0.0085% Fe), decomposition began at 400°, and the reactions (1), (2), (3a), (4), and (5) were involved. Ag is a good catalyst as it accelerated the desired decomposition (1) very strongly. With Pt, as a fine screen, decomposition began at 500°, and the reactions (1), (2), (3a), (3b), (4), and (6) were involved. Pt differed from Ag essentially in accelerating decomposition (4), besides (1), and it is not suitable as contact or material of construction. With Al gravel, surface oxidized, decomposition began below 300°, and the reactions (2), (3a), (3b), and (4) were involved. The decomposition (2) was accelerated almost exclusively, and Al is not suited for use, but it is a good catalyst for the preparation of Me₂O from MeOH, and possibly for the synthesis of Me₂O from CO and H₂. With Cu, as shavings, decomposition began at 450°, and the reactions (1), (2), (3a), (4), and (5) were involved. Cu did not accelerate decomposition (1) selectively, and structural parts in contact with CH₂O formation cannot be made of Cu, but others operating below 400° can be made of Cu. With Fe, as wrought Fe shavings, decomposition began at about 550°, and the reactions (1), (2), (3a), (3b), and (4) were involved. Fe in itself is a good catalyst, accelerating decomposing (1) very strongly, but considerable acceleration of side reactions results in the covering of the Fe with C, and the material is not suitable for construction of an apparatus. With burned lime, decomposition began at about 450° and the reactions (1), (3b), (4), and (5) were involved, and all strongly accelerated. With compressed C, decomposition began at about 450°, and reactions (1) to (5) were all strongly accelerated, making C a very unsuitable material. Experimental results and 5 refs. are given.

——. See abs. 2296, 2297.

2021. KÜSTER, ——. [Synthesis of Hydrocarbons From Carbon Monoxide at Atmospheric Pressure Under the Influence of Catalysts of the Iron Group.] Génie civil, vol. 109, 1936, pp. 438–439.

2022. KÜSTER, H. [Literature Review of the Synthesis of Formaldehyde From Water Gas.] Brennstoff-Chem., vol. 17, 1936, pp. 103–109; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 298–310.

43 literature and 30 patent refs.

2023. ——. [Reduction of Carbon Dioxide to Higher Hydrocarbons at Atmospheric Pressures by Catalysts of the Iron Group.] Brennstoff-Chem., vol. 17, 1936, pp. 221–228; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 277–292; Chem. Abs., vol. 31, 1937, p. 1581.

Conversion with CO₂–H₂ mixtures has been effected at 200°–300° in one stage. Hydrocarbons formed are similar to those obtained in the benzine synthesis with CO and H₂. The intermediate formation of CO is indicated in the reaction mechanism. The reducing, hydrogenating, and polymerizing effects of the catalyst are influenced by impregnation of the unreduced catalyst with K₂CO₃. Results obtained by various single, double, and triple combinations of Co, Fe, Cu, Ni, Al, and Th are compared. Conversion and products are shown graphically for 20° intervals.

2024. ——. [Reduction of Carbon Dioxide to Methane Upon Iron Catalysts at Ordinary Pressures.] Brennstoff-Chem., vol. 17, 1936, pp. 203–206; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 270–277; Chem. Abs., vol. 30, 1936, p. 7790.

Contrary to Sabatier, pure Fe at temperatures above 300° permitted conversion of CO₂ to CO and CH₄, the last in very small yield. Addition of small amounts of Al or Mn did not affect activity of the Fe. Cu and Co are practical activators. The hydrogenating characteristics of Ni appear evident even with 5%. With Co added, higher gases and liquid hydrocarbons are formed. 12 refs.

——. See abs. 987, 1831, 2621.

KVALNES, H. M. See abs. 150.

2025. KWAN, T. Adsorption of Carbon Monoxide on Platinum Catalyst. Jour. Research Inst. Catalysis, vol. 1, 1949, pp. 110–116; Chem. Abs., vol. 44, 1950, p. 4304.

CO adsorption isotherms were measured at pressures between 0.001 and 1 mm. Hg at 180°, 200°, 280°, and 300°. The differential heat of adsorption is constant for all quantities adsorbed and equals 11 kcal. per mol. By developing, on a statistical-mechanical basis, an expression for the change in heat of adsorption with fraction of surface covered by adsorbent, assuming that adsorption occurs without dissociation or that CO is dissociated to C and O, better agreement was obtained between observed and calculated values for the latter case.

2026. ——. Adsorption of Hydrogen on Nickel, Cobalt and Platinum at Low Pressures. Jour. Research Inst. Catalysis, vol. 1, 1949, pp. 81–94; Chem. Abs., vol. 44, 1950, p. 4304.

Adsorption isotherms of H at pressures between 10⁻³ and 1 mm. Hg on Ni, Pt, and Co powders and 50°–300° were determined with special care for absence of adsorption-desorption hysteresis. Surface areas of the samples were determined by the Brunauer-Emmett-Teller method. Initial H adsorption occurs at constant differential heat of adsorption equal to 26, 18, and 19 kg.-cal. per mol. for Ni, Pt, and Co, respectively, at 300°. After about 0.1 of the surface is covered, there is a gradual decrease in the heat of adsorption. On statistical-mechanical considerations an expression was derived for the relation between the differential heat of adsorption on H and the fraction of the sorbent surface covered. Comparison between observed and calculated data for this relation shows satisfactory agreement and is interpreted to mean that the Brunauer-Emmett-Teller measured surfaces of these materials are homogeneous and completely available for H adsorption.

2027. ——. Research on Pure Iron and Synthetic Ammonia Catalyst by Means of Hydrogen Adsorption. Jour. Research Inst. Catalysis, vol. 1, 1949, pp. 100–109; Chem. Abs., vol. 44, 1950, p. 4304.

Adsorption isotherms of H at pressures between 10⁻⁴ and 1 mm. Hg on pure Fe and synthetic NH₃ catalyst were determined at 0°, 25°, 50°, and 100°. Differential heats of adsorption diminish continuously from 17.5 kg.-cal. per mol. at the lowest pressure to 5 kg.-cal. per mol. at the highest pressure. Calculations from the rate of decrease of the differential heat of adsorp-

2028. ——. Adsorption of Carbon Dioxide on Reduced Nickel. Jour. Chem. Phys., vol. 18, 1950, pp. 1309–1310; Chem. Abs., vol. 45, 1951, p. 18.

Adsorption isotherms are derived for the adsorption of CO₂ as CO₂, CO+O₂, and C+2 O. Experimental evaluation was accomplished at 150° and 200°, with equilibrium pressures 0.001–0.1 mm. Hg. The differential heat of adsorption was almost constant at 22 kg.-cal. per mol. The experimental values for fraction of surface covered agreed best with the isotherms for complete dissociation. Experiments on reduced Co gave similar results.

KWANTES, A. See abs. 1739.

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2029. LACHINOV, S. S. [Reduction of Iron Catalysts Used in the Synthesis of Ammonia. I. Investigation of the Reduction Process.] Jour. Appl. Chem. (U. S. S. R.), vol. 10, 1937, pp. 19–34 (in German, pp. 34–35); Chem. Abs., vol. 31, 1937, p. 4457.

"L-1" Fe catalyst is not completely reduced by the N-H mixture below 475°, though the reduction process may cease in the presence of O adsorbed by Fe. The velocity of reduction increases with the increase of temperature, according to the Arrhenius law $lnK = C - (A/RT)$, where K is the velocity constant, A is the change of the energy in calories, and C is an integration constant. The following formulas can be used for all practical purposes: (1) $px^{0.32} = 1,000$, at $p = 100$ atm. and Cv = 15,000 cal. and (2) $px^{0.117} = 805$, at $p = 100$ atm. and Cv = 30,000 cal., where y is temperature and x is time in hours; both formulas represent a parabolic relation between temperature and time. The velocity of the reduction of an Fe catalyst also increases with increase of the volume velocity of the stream of N-H mixture and can be represented for the "L-1" catalyst by a straight line at the velocity of 1,000–10,000, by a parabola at 10,000–25,000, and by a hyperbola at 25,000–90,000. The general equation for this catalyst at $p = 100$ atm. and $t = 375°–500°$ is $(15.8x + y - 11,522)(8.6 \times 10^{-4} \cdot x^{2.32} - y) - (0.6x^2 - 196x + 20,120 - y) = 0$, where x is the time of reduction in hours, and y is the volume velocity. The velocity of reduction increases first with increase of the pressure, but the increase of the pressure inhibits the reduction at the end of the process. 12 refs.

2030. LACHINOV, S. S., VVEDENSKII, A. A., AND TELEGIN, V. G. [Reduction of Iron Catalysts Used in the Synthesis of Ammonia. II. Influence of the Reduction Conditions on the Activity of the Catalyst.] Jour. Appl. Chem. (U. S. S. R.), vol. 10, 1937, pp. 435–455 (in German, p. 456); Chem. Abs., vol. 31, 1937, p. 7201.

High reduction temperature of the "GIVD-L-L" catalyst (containing: FeO, 21.90; Fe₂O₃, 71.48; K₂O, 1.90; Al₂O₃, 4.05; SiO₂, 0.10; MnO, 0.41; S, 0.03; and P, 0.01%) at constant pressure and volume velocity, has a negative influence on the activity of the catalyst. The volume velocity of the H₂-N₂ mixture has a positive influence on the activity of the catalyst. The pressure (within 1–300 atm.) has only slight negative influence upon the activity of the catalyst, which can be neutralized by corresponding increase of the volume velocity. A method of reduction of the catalyst was worked out, consisting of a stepwise increase of the temperature from 360°–500°, keeping the catalyst at 360°, 380°, 400°, 425°, 450°, 475°, and 500° for complete separation of H₂O at each temperature, and maintaining the highest possible partial pressure of H₂ and the best H₂O vapor condensation. Further investigation is required for improvement of the method.

2031. LACHINOV. S. S. [Reduction of Iron Catalysts Used in the Synthesis of Ammonia. III. Duration of the Complete Reduction of the Catalyst and Its Activity in Relation to Its Composition, the Regimen of Smelting and the Conditions of Reduction.] Jour. Appl. Chem. (U. S. S. R.), vol 10, 1937, pp. 1847–1866 (in French, pp. 1866–1867); Chem. Abs., vol. 32, 1938, p. 2208.

All conditions of reduction that lead to the accumulation of H₂O vapor in the gas phase above the catalyst increase the duration of reduction and lower the catalytic activity. The harmful action of H₂O vapor upon the activity of the catalyst is explained by the development of the oxidation-reduction processes, which caused the recrystallization of the contact surface. An increase of the volume velocity of gas mixture decreases the duration of the reduction and increases the activity of catalyst, but only to a certain limit, after which, a further increase of the volume velocity has no effect. The velocity of the reducing-gas stream at which H₂O vapor is removed as fast as formed permits reduction in the shortest time and produces the most active catalyst. An increase of temperature, all other conditions being equal, decreases the duration of complete reduction of catalyst and lowers its activity, but increase of the volume velocity of gas mixture decreases the harmful effect of increased temperature. An increase of pressure during the reduction lowers the activity, but an increase of the volume velocity decreases or completely neutralizes this effect. A slight increase of temperature and duration of smelting of the catalyst increases the duration of reduction. Oxidation of Fe under O₂ pressure with an admixture of activators yields a highly active and stable catalyst, in spite of the presence of 1.5% SiO₂. The Fe-Mo catalyst, prepared from a ferromolybdate by oxidation smelting with the K₂O-Al₂O₃ admixture, is not easily reduced, and has an average activity and high stability. Admixture of oxides of Cu or Ni to this catalyst decreases its activity. 40 refs.

2032. ——. [Conference on Heterogeneous Catalysis. Moscow, May 13–16, 1940. Analysis of the

Process of Reduction of Ammonia Catalysts.] Jour. Phys. Chem. (U. S. S. R.), vol. 14, 1940, pp. 1260–1270; Chem. Abs., vol. 35, 1941, p. 3882.

Various data on the reduction of Fe_2O_3, Fe_3O_4 with 2–5% K_2O and Al_2O_3 at temperatures up to 500° and pressures up to 300 atm. are discussed. The reduction of an activated catalyst proceeds 5–6 times as fast; the activators aid in the formation and stabilization of the active centers. The reduction takes place in an induction, an autocatalytic and a residual-reduction period.

2033. LACHINOV, S. S., AND TELEGIN, V. G. [Activity and Stability of Iron Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), No. 12, 1934, pp. 31–33; Chem. Abs., vol. 29, 1935, p. 2311.

Al_2O_3. MgO, and SiO_2 activate Fe catalysts but do not make them stable. K_2O renders them stable but gives decreased activity. K_2O and SiO_2 together form a good activator, but the catalyst is quite unstable. K_2O and Al_2O_3 or MgO and SiO_2 give a very stable catalyst. Mechanisms of activation are discussed.

2034. LACHINOV, S. S., AND TELEGIN, V. G. [Iron Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), No. 5, 1934, pp. 30–32; Chem. Abs., vol. 28, 1934, p. 5605.

Addition of about 10% K_2O to Fe_2O_4 lowers the activity of this catalyst, though small amounts of both K_2O and MgO increase the activity. These effects are due to the alkalinity of the added compounds, which causes more rapid desorption of the NH_3. Catalysts containing K_2O are easily decomposed by air. Addition of K_2O and Al_2O_3 increases the stability of the catalyst toward heat.

LACHINOV, S. S., VVEDENSKII, A. A., AND TELEGIN, Y. G. [Reduction of Iron Catalysts Used in the Synthesis of Ammonia. II. Influence of the Reduction Conditions on the Activity of the Catalyst.] See abs. 2030.

2035. LACY, B. S., DUNNING, R. G., AND STORCH, H. H. Equilibrium in the Synthesis and Decomposition of Methanol. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 926–938; Chem. Abs., vol. 24, 1930, p. 2943.

Average equilibrium constants for the reaction $2 H_2 + CO = CH_3OH$, measured at 300° and 250° from both sides, at 200° from the synthesis side, all at 50 atm. pressure, were 1.9×10^{-4}, 1.25×10^{-3} and 3×10^{-2}, respectively, and 1.8×10^{-3} at 250° and 20 atm. from the synthesis side. Similar constants were found by calculations, using the reactions of $HCOOMe$ and H_2 and of MeOH and CO. (See abs. 560, 2448, and 3209.)

2036. LAHIRI, A. Synthetic Oil From Coal. I. Jour. Sci. Ind. Research (India), vol. 7A, 1948, pp. 357–361; British Abs., 1949, B, I, p. 29.

Describes production of synthetic oil and gasoline from coal by various hydrogenation processes.

2037. ———. Synthetic Oil From Coal. II. Fischer-Tropsch Process. Jour. Sci. Ind. Research (India), vol. 7, A, 1948, pp. 406–411; British Abs., 1949, B, I, p. 233.

Reviews development of the process and discusses inherent advantages and difficulties. Analyzes recent developments, which have been concentrated on the problem of heat transfer. Catalysts are now introduced at a constant rate in the fluidized condition and plants contain internal heat exchangers. Heat of reaction is removed by evaporating oil introduced with the synthesis gas. The gasification of coal and coke by the Bubiag-Didier, the Thyssen-Galocsy, and the Pintsch-Hillebrand processes are summarized.

2038. ———. Synthetic Oil From Coal. III. Economics of Synthetic Oil Manufacture. Jour. Sci. Ind.

Research (India), vol. 7, A, 1948, pp. 442–446; British Abs., 1949, B, I, p. 336.

Discusses in detail products and economics of the hydrogenation and Fischer-Tropsch processes for the manufacture of petroleum from coal; it is stressed that the 2 processes are complementary. Reviews present position regarding raw materials in India, with particular reference to the quality of coal, and considers the economic prospects of the 2 processes.

——— See abs. 1771a.

2039. LAHIRI, D. Liquid Fuels From Water Gas. Sci. and Culture, vol. 3, 1938, pp. 670–673; Chem. Zentralb, 1938, II, p. 1521.

Special attention is paid to synthesis by Fischer-Tropsch process.

2040. LAHUERTA, P. [Literature Referring to Fischer-Tropsch Synthesis.] Combustibles (Zaragoza), vol. 6, September–December 1946, pp. 126–134.

2041. LAIDLER, D. S., AND TAYLOR, J. Study of the Carburization Process With Special Reference to Gas Carburizing. Reduction of the Carbon Dioxide Content of Town Gas. Jour. Iron Steel Inst. (London), vol. 165, 1950, pp. 23–39; Chem. Abs., vol. 44, 1950, p. 9890.

Carburization process with town gas as the carburizing medium has been developed. In purified town gas or in CO, all the atomic C formed at the surface is absorbed into the steel. The rate of diffusion of C in the steel and the rate of graphite formation are the rate-controlling reactions. With town gas containing O_2, moisture, and CO_2 there are 3 important differences: Soot forms at the surface at the expense of atomic C. The soot so deposited restricts further carburization. Formation of graphite from atomic C is rapid and is no longer the rate-controlling reaction. In a gas containing 2.6% CO_2, 0.8% O_2, 2.6% $C_n H_m$, 24.7% CH_4, 48.3% H_2, and 12.3% N_2, the O_2 and CO_2 contents are decreased by passing the gas over a baryta catalyst. 16 refs.

LAIDLER, K. J. See abs. 3180.

LAMBERT, G. I. See abs. 3591.

2042. LAMBRIS, G. [Deposition of Carbon in the Electrolysis of Nickel From Solutions.] Ztschr. Elektrochem, vol. 15, 1909, pp. 973–981; Chem. Abs., vol. 4, 1910, p. 866.

Previous work upon the electrolytic deposition of C is reviewed and the author's experiments are described in detail. Various C-containing baths of Ni were used and the deposited Ni and gases analyzed. The gases in 1 of the experiments were: CO_2, 6%; hydrocarbons (heavy), 1.2%; hydrocarbons (light), 2.6%; air, 4.8%; H_2, 89.9%; total 99.1%. These values are about the same for several experiments. It is shown that the colloidal theory for the deposition of C does not hold good and that C_2H_2 plays a large part in the deposition. The conclusions given are: (1) The absorption of C by the Ni is entirely due to a gas reaction. (2) The gases that will introduce C into the Ni are CO, CO_2, and C_2H_2. Gases reduced beyond C_2H_2 do not introduce any. (3) Oxalic acid is partly reduced to C_2H_2 upon Pt and Ni, but not when Cu, Fe, or Sn cathodes are used. Therefore C_2H_2 is the only carrier of C to metals in electrolysis. (4) The C in electrolytic Ni is present in the form of carbide.

2043. LAMECK, P., AND NIEBHAUS, H. [Utilization of Coal.] Stahl u. Eisen. vol. 57, 1937, pp. 1041–1048, 1074–1079; British Chem. Abs. 1937, B, p. 1152.

Discussion of the progress since 1934 in coal preparation, coking, carbonization, hydrogenation, gas purification and utilization, benzine synthesis, etc.

2044. LAMECK, P., AND SCHEER, W. [Coal Improvement—Fischer-Tropsch Process.] Stahl u. Eisen. vol. 61, 1941, pp. 63–66, 86–90, 109–112; Chem. Zentralb. I, 1941, p. 3029.

Report for 1937–39 on statistics on coking, briquetting, gas purification, high-pressure hydrogenation, Fischer-Tropsch, gasification, and low-temperature carbonization.

2045. LAMME, N. [Synthesis of Hydrocarbons According to Fischer-Tropsch.] Thesis, Tech. High School, Delft, Holland, Feb. 20, 1946, 207 pp. (in Dutch); Chim. et ind., vol. 56, 1946, pp. 213–214.

2 catalysts were utilized by the author in his investigations; the Raney skeleton catalyst of Ni-Co and the precipitated $Co-ThO_2$-kieselguhr catalyst of Fischer. In the synthesis, at atmospheric pressure, the best results were obtained by first reducing the catalyst and then heating it in an atmosphere of CO. The catalyst in any case does not become active until after 5–10 days use, then it maintains its activity for 30–50 days. The yield of product is about 50%; the ratio of oil to gasoline is about 1:1, depending upon the synthesis temperature. The catalyst is regenerated by means of H_2. 1/3 of the reaction gas mixture is transferred into liquid and solid hydrocarbons, 1/3 into gaseous hydrocarbons, and the remainder is not converted. At a higher temperature, a higher transformation takes place but in the form of gaseous hydrocarbons. Under 10 atm. pressure and with the $Co-ThO_2$-kieselguhr catalyst the average molecular weight of the hydrocarbons formed is the same as that of the hydrocarbons obtained at atmospheric pressure. The synthesis of CH_4 also is increased, and larger amounts of CH_4 and CO are found in the residual gases. In the reduction of CO_2 by H_2 it is found that CO acts as a catalyst poison. The hydrocarbons formed are mostly C_3 and C_4, their amount diminishing as the molecular weight increases; for a hydrocarbon of definite molecular weight, an increase in quantity keeps pace with the diminution in saturation. There is no formation of cyclic compounds in the Fischer-Tropsch process.

2046. LAMP. Synthetic Gasoline. Vol. 29, No. 2, March 1947, pp. 7–11.

Development and present status of the synthesis process for producing gasoline from gas are discussed with special emphasis on the so-called fluid catalyst process of the Standard Oil Development Co. The reduction in the number of reactors for a 10,000-bbl.-per-day plant from 128 in the Fischer-Tropsch process to 4 in the fluid process is considered one of the outstanding achievements in its development. Even so, the heavy initial investment involved and the rigid location requirements will inevitably limit the number of commercially feasible synthesis plants. The commercially available potential reserve of synthetic gasoline from sources other than natural gas, such as coal, tar sands, and oil shales, is pointed out also. Whereas production of synthetic gasoline from these sources is not at present attractive commercially, it will become more competitive as research continues. The quantities of gasoline that could be brought into commercial production from each of the above sources, would, of course, depend upon the service station price range per gal. For instance, a price of up to $0.26 would make marketable 300 billion bbl. from coal and 1 billion from tar sands; $0.26–$0.31, 18 billion bbl. from oil shales, 3,500 billion from coal, and 2 billion from tar sands; $0.31–$0.36, 38 billion bbl. from oil shales, and 2 billion from tar sands; and over $0.36, 45 billion bbl. from oil shales.

2047. LANDA, S. Synthetic Fuel in Europe. Petrol. Eng., Refining Gas Processing sec., vol. 21, No. 11, October 1949, p. A–58.

Abstract of a paper presented at United Nations Resources Conference. Review of synthetic-fuel production in Europe, with particular reference to the methods developed in Germany and other central European countries by hydrogenation and synthesis. Discusses factors influencing the economic operation of synthetic fuel plants, and estimates capital requirements and operating costs. Prospects for further development of the industry are considered excellent.

2048. ———. Possibilities and Costs of Synthetic Fuels. Petrol. Eng., vol. 22, January 1950, pp. A53–54, 56.

There are 2 general methods of obtaining synthetic fuels, pressure hydrogenation and complete synthesis from CO and H_2. Coal is given chief consideration for production of synthetic liquid fuels. Several factors influence production costs in producing synthetic fuels, such as the complicated installations, high labor cost, and the preparation of synthesis gas and hydrogen. It is possible, however, to effect economics in operation. Automatic devices have already been introduced, which not only reduce labor costs but insure more efficient operation as well.

2049. LANDER, C. H. Recent Developments in the Science of Coal Utilization. Mech. Eng., vol. 49, 1927, pp. 1–11; Chem. Abs., vol. 21, 1927, p. 811.

Results obtained during the past few years from the scientific researches on coal are reviewed and discussed in relation to their engineering problems and practical applications. Among the subjects treated are: The constitution of coal; low-temperature carbonization; low-temperature coke and tar; metallurgical coke; synthetic fuels from CO and H_2 by the Patart and Fischer-Tropsch processes; hydrogenation of coal; and furnace design.

2050. ———. Treatment of Coal to Produce Liquid Fuels. Bull. Liverpool Eng. Soc., vol. 6, No. 6, 1933, pp. 17–22.

Discusses low-temperature carbonization, direct hydrogenation of coal with flowsheet, and hydrogenation of CO.

2051. ———. Hydrogenation—Review of Early Difficulties. Proc. South Wales Inst. Eng., vol. 53, 1938, pp. 424–447; Chem. Abs., vol. 32, 1938, p. 6833. 11th Menelaus Memorial lecture.

2052. LANDGRAF, —. [Influence of an Increased Rate of Flow on the Olefin Content of Synthetic Gasoline.] FIAT Reel K 29, Frames, 7,172–7,183, 1938, PB 70,218.

Tests establish that an increase in the rate of flow causes a reduction of the olefin content of the gasoline produced and increases the exhaustion of catalysts. The olefin content of the oil produced is not influenced to a noticeable degree. 3 graphs, 1 picture, 2 tables.

2053. LANE, J. C. Fischer-Tropsch Potentialities of Public Utility Gas Companies. Gulf Research & Development Co., Chemistry Division Rept. 259, 1944.

Evaluation of public-utility gas companies of the United States with regard to their potentialities as manufacturers of synthine products. Only 8 of the 118 companies considered appear very likely to enter the field of synthetic liquid fuels.

2054. LANE, J. C., AND WEIL, B. H. Synthine Process. I. Introduction, Synthesis-Gas Production and Purification. Petrol. Refiner, vol. 25, 1946, pp. 355–366; Chem. Abs., vol. 42, 1948, p. 9118.

History and nomenclature of the Synthine (Fischer-Tropsch) process are traced. The ratio of H_2:CO in this process ranges 2:1–<1:1. The important methods for producing the water-gas mixtures are (1) standard manufacture from coke, (2) manufacture from low-volatile coal, (3) manufacture from coal or coke by using O_2 in the steam blast, and (4) conversion

of coke-oven gas with steam, either catalytically or noncatalytically. These methods, with some less conventional methods, are discussed in detail. Underground gasification of coal by (1) the chamber, (2) the stream, and (3) the percolation methods is discussed in some detail. Synthesis gas can be obtained also by means of the reaction: $CH_4 + H_2O \rightarrow 3H_2 + CO$ or $CH_4 + CO_2 \rightarrow 2CO + 2H_2$. Yields, catalysts, and manufacturing procedures are given for these two reactions. Controlled oxidation of CH_4 to give H_2 and CO also is economical, and catalysts and reaction conditions are discussed. Regardless of its source, synthesis gas must be purified of S and its compounds. The H_2S is removed first by ethanolamine, ferric oxide, or other methods, and then the organic S compounds are catalytically oxidized and removed. Patents and processes for this purpose are reviewed.

2055. ——. Synthine Process. II. Catalytic Synthesis, Including Catalysts and Reaction Mechanisms. Petrol. Refiner, vol. 25, 1946, pp. 423–434; Chem. Abs., vol. 42, 1948, p. 9118.

Two main reactions take place in the synthine process, the predominant one depending chiefly on the ratio of $H_2:CO$ and the type of catalyst used: (1) $nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$; (2) $nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$. Since the reaction is exothermic and involves a reduction in volume, relatively low temperatures and elevated pressures favor the reaction. Temperatures range from 375° with Ni or Co catalysts to 465° with Fe catalysts, and pressures vary from atmospheric pressure to 150 p. s. i. The synthesis gas is passed through reaction chambers in 1 or more stages, with or without recycle of the unconverted portion. The heavier products are condensed from the residual gas, and the lighter products are adsorbed on charcoal or in oil. Most theories of the reaction mechanism stipulate the intermediate formation of carbides of the catalyst metals. By hydrogenation of these unstable carbides, CH_2 groups are produced, but there are various theories as to the method of producing them. Both polymerization and hydrogenation then occur to produce hydrocarbons of higher molecular weight. Catalysts consist of Fe and Co alone, or in mixtures with Ni. They are supported on an inert carrier (kieselguhr), or used as all alloy-skeleton type catalysts, or fluid catalysts. The German commercial operation is described. The various modifications in the process that will produce branched-chain hydrocarbons, alcohols, aromatic hydrocarbons, or CH_4 are all discussed in detail.

2056. ——. Synthine Process. III. Products, Byproducts, and Special Topics. Petrol. Refiner, vol. 25, 1946, pp. 493–504; Chem. Abs., vol. 42, 1948, p. 9119.

Primary products are almost entirely straight-chain paraffinic and monoölefinic hydrocarbons. Aromatic compounds and naphthenes are present in only negligible amounts. The yield of oxygenated compounds ranges from almost zero to several %. The hydrocarbons produced range from CH_4 to hard waxes. CH_4 yield is 10–15%. Medium pressure (150 p. s. i.) yields liquefied petroleum gases, 7; gasoline, 38; diesel oil, 30; and wax, 25%. None of the processes gives any oils with lubricant properties. Light products are recovered by adsorption on charcoal or absorption in oil. Residual gas consists of: CH_4, 30.9; H_2, 18.0; CO, 10.5; CO_2, 20.3; N_2, 18.5; and C_2H_4–C_3H_6, 1.6%. The heating value of this gas is about 395–425 B. t. u. per cu. ft. and is mostly burned as fuel. The C_3–C_4 fraction is used in the synthesis of polymer or alkylate gasolines, synthetic alcohols by sulfonation and hydrolysis, or is burned as fuel. Since gasoline from the Synthine process is low in octane number owing to its straight-chain paraffinic structure, it is upgraded by cracking before use. Diesel-oil fractions have a very high

cetane number, but are improved by mixing with petroleum oils. Some of this fraction was used for Mersolate detergents. The paraffin waxes, consisting of a mixture of normal and isoparaffins with no cyclic hydrocarbons, were separated into soft, slab, and hard paraffins by distillation, pressing, and sweating. Lubricants have been made by polymerization of the olefins, alkylation, and condensation. Fatty acids are produced by oxidation of paraffin waxes, and esterification with glycerol gives some edible fats. Heavy synthine oils were sulfochlorinated and saponified to give detergents. Greases were made from oxidized paraffin waxes. Treatment of the Synthine olefins with H_2 and CO gives alcohols and aldehydes, and a small amount occurs as byproducts directly from the process. Miscellaneous chemicals produced in small quantity as byproducts are listed.

2057. ——. Synthine Process. IV. Basic Economics and the Current Situation. Petrol. Refiner, vol. 25, 1946, pp. 587–598; Chem. Abs., vol. 42, 1948, p. 9119.

Discusses economics of the process. It is predicted that the total investment cost for producing gasoline by the Synthine process with coal as the source of gas eventually will be $2,500/bbl./day. Steel requirements are high, and a plant could not be erected speedily in an emergency. With natural gas for the process, it cannot at present compete with refinery methods utilizing crude petroleum. Byproducts will help balance costs, however. A list of companies and organizations and their current situation in the Synthine process field is given. 360 refs.

LANG, A. See abs. 2773.

2058. LANG, W. A. Research in the Coal Industry in Canada. Canadian Min. and Met. Bull. 406; Trans. Canadian Inst. Min and Met., vol. 49, 1946, pp. 51–62.

3 methods are available for converting coal into oil: The Fischer-Tropsch synthesis from water gas; the Bergius direct coal hydrogenation; and the carbonization of coal followed by hydrogenation of the tars and light oils. The first process has become competitive with gasoline from petroleum when based on the utilization of natural gas as the raw material. It is thought, however, that the ultimate source of synthesis gas will be the lower-rank coals or a char produced from them. The use of efficient, continuous water-gas producers, made possible by the use of O_2 instead of air, would be a necessary development. The production of gasoline by direct hydrogenation of coal does not appear as hopeful of success as does the Fischer-Tropsch process because of the very high capital costs owing to the high temperatures and pressures used. Recent modifications, such as the extraction-hydrogenation processes of Pott-Broche and Uhde, which allow the use of lower pressures in the initial stages, may change this outlook. It also appears that partial hydrogenation of coal for the production of crude fuel oils and tar acids and for high-heat-value gas may do much toward solving the economic problem by lowering the costs of production materially. The amount of tar acids produced by this method is roughly 10 times the amount produced by carbonization. Much fundamental research is necessary on the reactions of coal hydrogenation. The production of coking coals from non-coking coals, and the production of CH_4, MeOH, etc. are also visualized as possible developments.

2059. LANGE, H., AND MATHIEU, K. [Progress of Austenite Transformation in the Undercooled State of Iron–Nickel–Carbon Alloys.] Mitt. Kaiser-Wilhelm-Inst. Eisenforsch Düsseldorf, vol. 20, 1938, pp. 125–134; 239–246; Chem. Abs., vol. 32, 1938, p. 7878.

Use of the thermomagnetic method in the study of steels is described. Explains magnetic balance.

2060. LANGER, A., AND FOX, R. E. Mass-Spectrometer Analysis of Some Oxygen-Containing Compounds. Anal. Chem., vol. 21, No. 9, 1949, pp. 1032–1035.

In an attempt to analyze some oxygenated compounds by means of the mass spectrometer, using the same procedures as in the analysis of gaseous and liquid hydrocarbons, several difficulties were encountered. Extremely long evacuation times were necessary to remove some compounds from the tube, and, even more serious, large variations in peak heights occurring in successive scanning of the sample indicated that the instrument was unable to maintain calibration. Some of these difficulties were partly overcome by using a heated tube and a new trap design. Results obtained with mixtures of MeOH, formic acid, methyl formate, and methylal are included. In general, the results do not attain the precision and reproducibility of hydrocarbon analyses.

LANGER, C. See abs. 2306.

LANGHEIM, R. See abs. 1949, 1955.

LANGLEY, W. D. See abs. 1488.

LANIN, V. A. See abs. 1789.

2061. LANNING, H. J., AND CLARK, G. C. Manufacture of Fatty Acids by Oxidation of Paraffins, Hydrogenation of the Fatty Acids at I. G. Farbinindustrie A.-G., Ludwigshafen-Oppau. BIOS Final Rept. 748, September 1946, 21 pp., PB 47,720.

As raw material for the production of fatty acids, synthetic paraffins obtained from hydrogenation of CO or from low-temperature carbonization of lignite were used. The average melting point of the paraffins is 30°–50° and the average chain length C_{18}–C_{20}. Oxidation was carried out with potassium permanganate. Production and labor costs and yields are given; also flowsheets.

LAPSHIN, S. I. See abs. 3763, 3764, 3766.

2062. LARIN, A. Y. [Cracking of Heavy Petroleum Stocks Over Heated Surfaces.] Bull. acad. sci. U. R. S. S., classe sci. tech. 1944, pp. 42–47; U. O. P. Co. Survey Foreign Petroleum Literature, Transl. 495; Nat. Petrol. News, vol. 38, No. 14, pp. R 286, R 288–289, 1946.

Heavy paraffin hydrocarbons obtained from CO and H_2 (Kogasin) are known to decompose under the action of a heated wire spiral immersed in them, forming a gas abundant in olefins. This method was used in cracking heavy-oil distillates containing paraffins, also naphthenes and aromatics, as well as heavy resinous substances. A gas was produced of a composition approximately identical with that obtained from paraffin wax. However, the yields of gas per unit energy consumed are lower, when the charge is richer in compounds with a low H content. An oil distillate consisting essentially of naphthenes gives a yield of gas per kw.-hr. that is half that obtainable from paraffin wax, whereas 1 containing up to 21% aromatics gives about ¼ as much. From fuel oils the yields of gas are still lower and fluctuate greatly depending upon the contents of resins and carboids in the charge.

2063. LARSON, A. T. Ammonia and Methanol Catalysts. Trans. Electrochem. Soc., vol. 71, 1937, pp. 346–351; Chem. Abs., vol. 31, 1937, p. 3644.

MeOH catalysts are reactive at appreciably lower temperatures than NH_3 catalysts. One of the earliest commercial catalysts for NH_3 was Fe to which was added a small % of a promoter such as oxides of the alkaline earths. Generally speaking, most MeOH catalysts have operating temperatures 350°–400°. NH_3 is the only product of the interaction of N_2 with H_2, but the products of the interaction of CO and H_2 are numerous, often depending upon the catalyst used. Thus, for example, a mixture of ZnO and Al_2O_3 as catalyst will produce Me_2O, and a mixture of ZnO and

Cr_2O_3 will confine the product to MeOH over a wide range of temperature. S has a serious, poisonous effect on the Fe catalysts for NH_3, but has no effect on the ZnO–CR_2O_3 catalyst for MeOH.

2064. LARSON, A. T., AND BROOKS, A. P. Ammonia Catalysts. Ind. Eng. Chem., vol. 18, 1926, pp. 1305–1307; Chem. Abs., vol. 21, 1927, p. 802.

Fe, Co, Ni, W, and Mo have been studied in the temperature range 450°–550° as NH_3 synthesis catalysts. Ni and Co were found inactive; at 550° W and Mo were the most active, and at 450° Fe and a mixture of Fe and Mo. The studies with Fe included a study of the promoter action of 16 difficultly reducible oxides added singly to the Fe. Only 5 of these oxides of Al, Si, Zr, Tl, and Cl had any promoter action under the conditions used. Mixing these oxides showed that when the oxides are closely related chemically, the combined effect is about the same as that given by each constituent. If the oxides differ considerably in their basic or acidic properties, the promoter action of the mixture is greater than that of either constituent alone. Promoters of mixtures of potash-alumina, potash-silica, and potash-zircon produced very active Fe catalysts.

2065. LASHAKOV, L. M. [Calculation of the Equilibrium $2H_2 + CO \rightleftharpoons CH_3OH$.] Acta Physiochim, U. R. S. S., vol. 11, 1939, pp. 849–860; Chem. Abs., vol. 34, 1940, p. 4648.

By means of the constants of the Beattie-Bridgeman equation of state, the specific volumes and fugacities of the $2H_2 + CO \rightleftharpoons CH_3OH$ system are calculated at temperatures from 250°–350° and pressures from 100–200 atm. By a graphical method, from the Newton-Dodge equation (abs. 2457) the equilibrium concentrations of CH_3OH are found to be much lower than those obtained on the basis of the ideal gas laws; the values agree well with the experimental data of Newitt, Byrne, and Strong (abs. 2448) and of Wettberg and Dodge (abs. 3583).

2066. LATEGAN, P. N. Possibilities of Establishing a Coal-Oil Industry in South Africa. Jour. South African Inst. Eng., vol. 29, 1930, pp. 23–28; Chem. Abs., vol. 26, 1932, p. 1416.

Outline of the Fischer and the Bergius processes. Experiments have shown that South African coals will yield 120–150 gal. of petrol per ton.

2067. ——. Oil From Coal. South African Min. and Eng. Jour., vol. 51, 1940, pp. 625–627; Coke Smokeless-Fuel Age, vol. 2, 1940, pp. 258–259; Chem. Abs., vol. 34, 1940, p. 8218.

In the Fischer-Tropsch process, the yield of gasoline is 1 ton per 5–6 tons of coal processed; the economic unit is much smaller than for hydrogenation, but the thermal efficiency is about ½ that of the hydrogenation process. It is believed that relative costs of production would be about the same in South Africa as in Great Britain, cheaper raw material and labor being offset by higher capital cost. Construction of the smallest economic units in South Africa is recommended to gain data and experience. The Fischer process would involve the lower capital expenditure. Its synthesis gas forms the basis of other chemical industries. Coal mined in conjunction with torbanite is very suitable for the production of synthesis gas.

2068. ——. Production and Distribution of Petrol From Coal and From Imported Crude Petroleum. Jour. Chem. Met. Min. Soc. South Africa, vol. 51, 1951, pp. 297–318; Coke and Gas, vol. 13, 1951, pp. 385–390.

Comparison of the production costs of synthesis gas for the Fischer-Tropsch process by the Koppers suspension method, the Winkler fluidized bed method, and the Lurgi fixed bed method shows that the costs per

1,000 cu. ft. are respectively 15.33 d., 16.74 d., and 18.40 d. (the latter after allowing credit of 3 d. for byproducts). It is found that gasification costs represents 60-70% of the total cost of synthesis gasoline. Capital costs for these 3 types of plants in South Africa capable of producing 300 million cu. ft. of gas per day are, respectively, £8 million, £5.6 million, and £15.3 million, not including £3 million for an O₂ plant. There are 3 methods for carying out the synthesis reaction: The fixed-bed system, the liquid-medium system, and the fluidized system. The total estimated cost for a complete oil-from-coal plant including a Koppers gasification, an O₂ plant, and a synthesis plant of 100 million gal. annual capacity will be £27 million or 1 s. 5 d. per gal. The estimated costs of gasoline from imported crude refined in a Rand refinery of 100 million gal. annual capacity costing £11,500,000, including the cost of a pipe line from the coast to the refinery, is 10.5 d. per gal. Allowing a return of 10% on the total capital investment the selling price amounts to 1 s. 1.25 d. per gal., compared with 1 s. 11.5 d. for synthetic gasoline and 1 s. 10.75 d. for imported gasoline. Refinery gasoline is therefore 10.25 d. cheaper than synthetic gasoline and 9.5 d. cheaper than imported refined gasoline.

2069. Latta, J. E., and Walker, S. W. Commercial Application of Hydrocarbon Synthesis in the United States. Chem. Eng. Progress, vol. 44, No. 2, 1948, pp. 173-176; British Abs., 1948, B I, p. 279.

Some of the problems encountered in the commercial development of the hydrocarbon synthesis are discussed, and a general summary of the lines along which process design and engineering on the proposed plants at Hugoton and Brownsville are proceeding is presented. Pilot-plant operation has disclosed the best reaction system and the knowledge obtained will be applied to the commercial operation of the enlarged plants, although much research work will still be required to determine the operability of the fluid Fe catalyst process and to resolve the many reaction variables involved in the changeover to large-scale operation.

Laughrey, P. W. See abs. 3311.

Launer, P. J. See abs. 420a.

2070. Laupichler, F. G. Manufacturing Costs of Gases for Ammonia Synthesis. Gas World, vol. 105, 1936, pp. 71-75; British Chem. Abs., 1936, B, p. 883.

Economics of the water-gas shift reaction are discussed.

2071. ———. Catalytic Water-Gas Reaction—Mass Transfer and Catalyst Activity. Ind. Eng. Chem., vol. 30, 1938, pp. 578-586; British Chem. Abs. vol. 32, 1938, p. 4866.

Equations are derived for mass transfer and reaction velocity in the catalytic water-gas reaction at constant temperature, which permit calculation of conversion rate for any given amount of catalyst, or the amount of catalyst required to obtain a given conversion. The equations are then extended to include the effect of gradually increasing temperature as found in commercial processes. The heterogeneous velocity coefficient obtained may be used to compare the activities of different catalysts. The effect of varying the initial temperature, steam : CO ratio, and flow rate were determined. The equations gave calculated values in good agreement with experimental determinations and are useful in determining the optimum conditions for operating catalytic converters.

Lauschke, G. See abs. 2928.

Lawton, G. See abs. 328.

Laxmann, A. See abs. 3060, 3062.

2072. Lazier, W. A. Hydrogenation of Carbon Oxides. 12th Rept., Committee on Catalysis, Nat. Research Council, 1940, pp. 120-130; Chem. Abs., vol. 34, 1940, p. 4968.

Review (83 references) discusses the synthesis of HCHO, MeOH, CH₄ and Kogasin from CO and H₂ and includes a list of recommended catalysts for the last named reaction.

2073. Lazier, W. A., and Adkins, H. Adsorption of Ethylene and Hydrogen by Zinc Oxide, Iron Oxide, Nickel and Copper. Jour. Phys. Chem., vol. 30, 1926, pp. 353-358; Chem. Abs., vol. 20, 1926, p 1545.

Measurements of the adsorption of H₂ and C₂H₄ at 22° and 74 mm. by catalysts were made in the usual constant-pressure adsorption apparatus. The catalysts were Cu, Ni, Fe₂O₃, and ZnO, made by several different methods. The volume of the gas adsorbed was measured by reference to the volume of N₂ required to fill the adsorption apparatus under comparable conditions. The catalytic activity of the catalysts was determined by measuring the decrease in gas volume after exposing the catalyst to equimolecular mixtures of H₂ and C₂H₄. The results of the adsorption and catalytic activity measurements indicate that there is a qualitative agreement between the 2 manifestations of chemical activity, but there is apparently no quantitative relationship between total adsorption and catalytic activity.

Leach, J. R. See abs. 654a.

Lecky, J. See abs. 53b.

2073a. Lecky, J. A., Hall, W. K., and Anderson, R. B. Adsorption of Water and Methanol on Coal. Nature, vol. 168, 1951, pp. 124-125; Chem. Abs., vol. 46, 1952, p. 11,630.

Results do not agree with a feature of the Ellis's theory of the structure of coal. The true surface area of coal is probably not measured by adsorption of MeOH and H₂O, since these polar compounds are not physically adsorbed in the usual sense, and hence are not amenable to the Brunauer-Emmett-Teller treatment for derivation of surface area.

2074. Le Clerc, G. [Catalytic Activity of Cubic Ferric Oxide in Synthesis of Hydrocarbons by Hydrogenation of Carbon Monoxide at Atmospheric Pressure.] Compt. rend., vol. 207, 1938, pp. 1099-1101; Chem. Abs., vol. 33, 1939, p. 1201.

Under normal conditions the limiting solid solution of K ferrite (formed by mixing K₂CO₃ and Fe(OH)₃), catalyzes the mixture CO+2H₂, yielding 45 gm. per m.³ of hydrocarbons solid or liquid at 15°. If the catalyst is prepared by adsorbing the K₂CO₃ by the Fe(OH)₃ the yield is raised to 80 gm. per m.³. The carbonates of Li, Na, Rb, or Cs give under similar circumstances the same yield and the same thermomagnetic curve. The solid solutions of ferrite in cubic Fe₂O₃ further show, in addition to the Curie point at 575° (that of magnetite), one at 250°. The conclusion that the active substance is the cubic Fe₂O₃ is confirmed by the alteration in yield if the cubic Fe₂O₃ is destroyed by heating above 500°. Thus, the action of the alkaline addition is to stabilize the cubic Fe₂O₃; the optimum temperature for such a catalysis is that of the second Curie point (250°)

——— See abs. 2080, 2081, 2276.

2075. Le Clerc, G., and Lefebvre, H. [Comparison of Catalytic Activity of Allotropic Varieties of Nickel.] Compt. rend., vol. 208, 1939, pp. 1650-1651; Chem. Abs., vol. 33, 1939, p. 5732.

Reduced Ni gradually loses catalytic power when the mixture CO+2H₂ is passed over it at 175°, but this is recovered on heating the Ni to 250° in a vacuum or in N₂. A similar loss of catalytic power is shown in the hydrogenation of C₆H₆ to C₆H₁₂ or of Me₂CO to Me₂CHOH. This loss of power is accompanied by transformation of the Ni from the ferromagnetic cubic to the nonmagnetic hexagonal form. No such loss of catalytic or magnetic power is shown in the similar transformation of Co; the change in Ni would, therefore, appear to be connected with a change in its electronic structure.

2076. Le Clerc, G., and Michel, A. [Mineral Chemistry—Preparation and Properties of the Hexagonal Form of Nickel.] Compt. rend., vol. 208, 1939, pp. 1583-1585; Chem. Abs., vol. 33, 1939, p. 5252.

Cubic Ni (I) heated at 170° for several days in CO is converted into the nonmagnetic variety (II). Thermomagnetic analysis of (II) shows a sudden appearance of magnetization at 250° with Curie point at 358°, and on cooling a further increase is shown. X-rays show (II) to be hexagonal with a=2.65 Å., c=4.32 (abs. 340), and the recovery of magnetization to be accompanied by reversion to the cubic form (I). This change is accompanied by a linear contraction of 5.4% (compared with 5.6% calculated.)

2077. Ledebur, A. Modification of Carbon in Iron. Jour. Iron Steel Inst. (London), vol. 44, II, 1893, pp. 53-76.

2078. Ledoux, E. Avoiding Destructive Velocity Through Absorbent Beds. Chem. Eng., vol. 55, No. 3, 1948, pp. 118-119; Chem. Abs., vol. 42, 1948, p. 3221.

Dimensionless expression is derived for the maximum safe mass velocity of the gas, G which will not cause motion of the adsorbent bed, with attendant reduction in size, owing to abrasion. The equation given is G₂=0.0167 Dgd_sd_a, where D is diameter of average particle, g is acceleration of gravity, d_g is density of the gas, and d_a is apparent density of the adsorbent bed. The constant, 0.0167, was determined from industrial experience.

2079. Lee, J. A. Esso's Fluid Catalyst Modifies Fischer-Tropsch. Chem. Eng., vol. 54, No. 10, 1947, pp. 105-107.

This paper describes certain of the modifications that are being made in the Fischer-Tropsch process by the Standard Oil Development Co. in the pilot plants at Baton Rouge. Natural gas is being processed to form liquid fuels and chemicals through use of the fluid catalyst. Results thus far have demonstrated satisfactorily the use of the fluid catalyst technique. It is found to be an excellent tool for securing uniform temperatures and high rates of heat transfer. Conversion and yield have been good. It is estimated that a synthesis plant to produce 8,300 bbl./day of gasoline having an A. S. T. M. unleaded octane no. of about 80 after mild treatment and 1,050 bbl./day of gas oil would cost about $35,000,000, exclusive of the equipment for recovery of oxygenated compounds. The method appears reasonably attractive from an economic standpoint at present.

Lefebvre, H. See abs. 2075.

2080. Lefebvre, H., and LeClerc, G. [Thermomagnetic Study of Iron Catalyzers for Hydrocarbon production by Fischer's Process.] Compt. rend., vol. 203, 1936, pp. 1378-1380; Chem. Abs., vol. 31, 1937, p. 936.

When CO+H₂ is passed over the catalyst (A) prepared by reduction in H₂ of the oxide precipitated by NH₄ or NaOH from solution of Fe(NO₃)₃, only gasoline is formed; if, however, about 1% K₂CO₃ is added the catalyst so formed (B), after an initial period of a few hours it produces heavy aliphatic hydrocarbons also. Thermomagnetic analysis gives for (A) a curve characteristic of magnetite, but for (B) one indicating a solid solution of KFeO₂ in cubic Fe₂O₃ (see abs. 2272). This is confirmed by the fact that K cannot be extracted from (B) by H₂O, but requires acid (for example, acetic) and that pure H₂ at 250° re-forms magnetite.

2081. ———. [Iron Catalysts in the Synthesis of Motor Spirit by Hydrogenation of Carbon Monoxide.] Compt. rend., Cong. chim. ind., 18th Cong., Nancy, September-October 1938, pp. 725-730; Chem. Abs., vol. 33, 1939, p. 6019.

Fischer synthesis can be carried out with Fe catalysts, those that are most frequently recommended containing small quantities of another metal together with alkali salts. Fe is active under two forms: magnetite and cubical Fe₂O₃, the latter producing much higher yields than the former. The presence of alkali is indispensable for the formation, under the conditions of the catalysis, of cubical Fe₂O₃; in the absence of alkali, only magnetite is stable. The function of the metal other than Fe is to facilitate the reduction that terminates the preparation of the catalyst and to favor the adsorption of a certain amount of the alkali salt during the preparation of the catalyst, thereby aiding indirectly in the formation of cubical Fe₂O₃.

2082. Lefol, J. [Liquid Fuels by Synthesis.] Carburents nat., vol. 4, 1943, pp. 137-141; Usine, vol. 52, 1943, No. 29; Chem. Zentralb., 1943, II, pp. 794 and 1773; Chem. Abs., vol. 38, 1944, p. 6065.

This lecture briefly reviews the possibility of manufacturing liquid fuels by carbonization, synthesis, hydrogenation, and fermentation of sugar from the hydrolysis of wood.

2083. Legrand, C., and Simonovitch, M. [Utilization of Coal With Particular Reference to the Production of Oil.] Publications Assoc. Ing. l'École de Mines de Mons., part 3, No. 62, 1937; Fuel, vol. 17, 1938, pp. 4-10, 41-47, 65-68, 96-104, 145-160, 217-221; Chem. Abs., vol. 32, 1938, p. 8743.

Survey and discussion of the technical development of the processes for the production of oil from coal by high- and low-temperature carbonization, by hydrogenation, and by synthetic processes. The Fischer-Tropsch process works at atmospheric pressure and at a temperature not normally exceeding 200° C. By keeping the temperature constant within limits of about 1° C., no CH₄ is obtained, but a mixture of liquid hydrocarbons and some solid paraffins. The temperature of reaction varies with the catalyst and the composition of the gas mixture; if rich in H₂, lower temperatures must be used. The production of synthetic gasoline from water gas is effected in the following stages:

(1) C+H₂O=CO+H₂—28.4 cal. This stage is endothermic.

(2) Removal of H₂S from the crude gas.

(3) Reduction of organic S content to 0.2 gm. per 100 m.³

(4) CO+2H₂=(CH₂)+H₂O+48 cal. This stage is exothermic. The catalysts used contain Fe, Ni, or Co, all of which form carbides. Mixed catalysts are more active and robust than single catalyst. The best catalyst is Co, followed by Ni and then Fe; the best mixed catalyst is Co-Th precipitated on kieselguhr. With Co a yield of 130 gm. of synthetic gasoline per m.³ of gas (CO+2H₂) can be obtained against a theoretical yield of 180 gm. The hydrogenation yields a mixture of oil and water in proportions varying between 1:1 and 1:2. The nearer the ratio of oil to water is to 1:1, the better is the yield of liquid products. With Co as catalyst the oil obtained contains 62% gasoline, 4% light products, 23% middle oil, and 11% paraffin (7% in the oil and 4% on the catalyst). The gasoline can be used directly in the motor without further purification because of its aliphatic nature. Its antiknock value can be raised in the usual way by adding tetraethyl lead. The middle oil is an excellent Diesel oil or it can be cracked into gasoline or may be used for making alcohol or lubricating oils.

2084. LEHRER, E. [Recording Apparatus for Determining the Magnetic Transition Points of Small Samples.] Ztschr. tech. Physik, vol. 10, 1929, pp. 177–185; Chem. Abs., vol. 23, 1929, p. 5063.

Discusses theory and possibilities of the instrument at some length. Curves are shown for Fe at various field strengths. Of the unusual applications are cited: Quantitative analysis of an Fe-cementite mixture (3% accurate), thermal decomposition of Fe₂N into Fe₄N. Gives preliminary data on the latter process.

2085. ——. [Equilibrium, Iron–Hydrogen–Ammonia.] Ztschr. Elektrochem., vol. 36, 1930, pp. 383–392; Chem. Abs., vol. 24, 1930, p. 4207.

Many experiments in which Fe was vitrified with H₂–NH₃ mixtures were carried out, and the resulting nitrides were examined by magnetic methods (abs. 2084). The equilibrium diagram of Fe–H–NH₃ showed four phases, α, γ, γ' and ε representing five divariant equilibria and two univariant with the phases α, γ, γ' or γ, γ' and ε as solid phases. 350°–750°. The α phase is a fixed solution of N in α-Fe, 0–0.5% N; the γ phase is a fixed solution of N in γ–Fe, 1–2.7% N; the γ' phase. Fe₄N mixed crystals 5.5%–6% N; ε phase 4.5–11% N. The dissociation pressures were calculated from the Haber values for NH₃ equilibrium. The dependence of the results upon the concentration of NH₃ showed that the γ' phase does not form in demonstrable amounts under normal working conditions.

2086. ——. [Magnetic Investigation of the System Iron–Nitrogen.] Ztschr. Elektrochem., vol. 36, 1930, pp. 460–473; Chem. Abs., vol. 24, 1930, p. 5192.

System Fe–N has been investigated and the results reported in numerous magnetism/temperature curves. 2 eutectoids are reported, at 591±4° and 650±4°, with a N content of 2.55±0.1% and 4.55±0.2%, respectively. The diagrams are interpreted.

2087. LEIBU, H. J. [Reduction of Iron Oxides by Hydrogen and Carbon Monoxide.] Schweiz. Arch. angew. Wiss u. Tech., vol. 14, 1948, pp. 1–19, 49–59, 76–85; Ind. Chemist, vol. 24, 1948, p. 267; Chem. Abs., vol. 42, 1948, p. 4881.

This study was carried out in 2 steps: (1) Determination of the best conditions for reduction in which the action of the gases on pure Fe₂O₃ of varying grain size and porosity was examined; (2) the same reduction process in the presence of other oxides forming the gangue and ores with a low % of Fe₂O₃. The action of H₂ is more effective than CO, being endothermic, while the latter is exothermic; it is about 3–4 times greater at 800°, but this ratio decreases at lower temperatures. At temperatures above 800°, CO disintegrates, forming CO₂ and C, so that Fe free from C cannot be obtained. The physical factors are similar in effect with both gases. Confirmation that H₂ eliminates S and O₂ simultaneously was not forthcoming; indeed, the elimination of O₂ is more rapid and that of S (with P), forms a different process. The reaction is influenced by the chemical composition and crystalline structure of the other oxides present, but their effect is only conspicuous if the ore consists of certain mixed crystals before or during the reaction. Under these circumstances the reaction is, thereby, not merely slowed down but is brought to a standstill, products being formed that resist reduction. Proof of this was obtained by spectral analysis. Reduction is virtually total (a) for ferrites (for example, 2 CaO.Fe₂O₃) where Fe is the active cation, while in other ferrites it is inactive; (b) for ferrites-where O₂ is combined mainly or solely with Fe (for example, FeO.MgFe). Reduction is more or less impossible: (a) In the presence of mixed crystals containing ferric or ferrous oxides in small quantities so that the groups (FeO₄), (FeO₄), are surrounded by crystals of alien cations, for example (Al, Fe)₂O₃, (Mg, Fe)O; (b) in the presence of intermediate crystals (SiO₄Fe₂) or (FeO₄Al₂) where the O₂ belongs not only to (FeO₄) or (FeO₄) groups but to the (SiO₄) or (AlO₆) groups as well.

LEIBUSH, A. G. See abs. 1670.

2088. LEIBUSH, A. G., AND BERGO, G. Y. [Reaction of Methane With Water Vapor. I.] Jour. Chem. Ind. (U. S. S. R.), vol. 15, No. 5, 1938, pp. 41–47; Chem. Abs., vol. 32, 1938, p. 7698.

Dynamic studies show that when a mixture of CH₄ and H₂O is heated for 1–8 sec, no C is formed below 900°, but when the mixture is heated under static conditions for 0.25–6 hr., C begins to form above 750° and disappears again above 950°. Increase in the amount of excess H₂O in the mixture, decrease in pressure, and the addition of O₂ decrease or stop C formation. These facts are explained by assuming that in a chain reaction CH₄ decomposes to CH₃, C₂H₆, C₂H₄, C₂H₂ and finally C, and that each of these compounds reacts to a greater or less degree with H₂O to give the final stable products, H₂, CO, and CO₂.

2089. ——. [Reaction of Methane With Water Vapor. II. Velocity of Reaction Between Methane and Water Vapor.] Jour. Appl. Chem. (U. S. S. R.), vol. 13, 1940, pp. 1003–1013 (in French, p. 1013); U. O. P. Co. Survey Foreign Petroleum Literature Index, Mar. 14, 1941; Chem. Abs., vol. 35, 1941, p. 1967.

Kinetics of the reaction of CH₄ with water vapor was investigated at 700°–1,050°. The initial stage of the process in a quartz vessel proceeded homogeneously and unimolecularly. Refractory clay and, especially, Ni catalytically accelerated the decomposition of CH₄. A decrease of initial partial pressure of CH₄ and an increase of an excess of water vapor also promoted decomposition of CH₄. The velocity of CH₄ decomposition diminished considerably with the formation of H₂. The relation between velocity and temperature is expressed by $K = 2.3 \times 10^9\, e^{-45000/RT}$ per min.

2090. LEIDHEISER, H., JR., AND GWATHMEY, A. T. Selective Deposition of Carbon on the (111) Face of a Nickel Crystal in the Catalytic Decomposition of Carbon Monoxide. Jour. Am. Chem. Soc., vol. 70, 1948, p. 1206.

Single crystal of Ni was carefully machined to a spherical shape and mechanically and electrolytically polished. Previous studies have shown that this treatment produces a smooth, strain-free surface whose crystalline orientation is the same as that of the bulk of the crystal. CO reacts with this surface and deposits C only on the (111) planes. The authors suggest that this specificity of the (111) plane for the reaction is due to the fact that most of the atoms of the basal plane of graphite can be made to coincide with little distortion with those of the (111) plane of Ni.

LEIPUNSKII, O. See abs. 65.

2091. LEITHE, W. [Determination of the Isoparaffin Content in Natural and Synthetic Soft and Hard Paraffins.] I. G. Farbenindustrie A.-G., Ammonia Laboratory Rept. 1615, May 13, 1939; FIAT Reel R 19, frames 6723–6740, PB 73,594; Meyer Transl. PC-S-IV, Wax Oxidation, vol. 3, 1949, chapter 56, pp. 49–56.

Method has been developed by modifying the Schaarschmidt reaction with SbCl₃ that permits determination of content of isoparaffins in soft and hard paraffin (number of C atoms about C₁₆–C₃₅) within an accuracy of 2–5%. The isoparaffin content was determined by the new method in many natural paraffins, as well as in gatsches and paraffins from the Fischer synthesis (at atmospheric and at medium pressure). The paraffins from the medium pressure synthesis showed, in contrast to Fischer gatsch obtained without pressure, a strikingly lower content of branched hydrocarbons and are, therefore, especially suitable for the preparation of soaps of slight odor by means of oxidation. The method thus offers a definite basis for evaluating paraffins with regard to their suitability for the preparation of soaps and edible fats.

2092. LELCHUK, S. L., BALANDIN, A. A., AND VASKEVICH, D. N. [Skeleton Catalysts and Their Application in Organic Chemistry.] Uspekhi Khim., vol. 14, No. 3, 1945, pp. 185–212; U. O. P. Co. Survey Foreign Petroleum Literature Index, Apr. 26–May 3, 1946, 17 pp.

Detailed study of alloyed and especially the so-called skeleton catalysts is needed, which may indicate new conditions for carrying out known reactions and help in developing catalysts for reactions that have not been effected. In this connection, the literature on the subject is reviewed, quoting 187 refs. The characteristics of these catalysts, methods suitable for their preparation, the connection between their structure and their catalytic activity, and the field of their applicability are discussed. They have been used successfully in hydrogenation of several types, dehydrogenation, H₂ disproportionation, isomerization, cyclization, dehydration, condensation, and oxidation. In the interaction of CO and H₂, formation of CH₄ must be prevented by maintaining conditions under which free CH₂ radicals are formed, which further interact to form hydrocarbons. Research on the methods of preparation by Fischer established that extensive leaching is favorable for the activity of these skeleton catalysts for the process in question and the most active catalysts contain Ni, Co, and Si. Tsuneoka and Murata conclude that when a catalyst of this type retains 4% Si, not removable by alkali, a molecular compound is apparently formed, and the assumption is justified that the compound not affected by leaching in the synthin catalyst is CoSi.

2093. LEMAIRE, E. [Synthesis of Fatty Acids by Catalytic Oxidation of Heavy Hydrocarbons: Their Application to the Manufacture of Soap and Edible Fats.] Génie civil, vol. 115, 1939, pp. 413–417; British Chem. Abs., 1940, B, p. 263.

Manufacture of soap and butter from coal consists of making fatty acids by oxidation of the heavy saturated paraffins obtained in the Fischer synthesis and then saponifying them to yield soap. A general survey is given of the constitution and properties of the fats and acids, and the process is traced by means of a flow diagram. The application of the synthetic fatty acids to the production of edible fats is said to have been accomplished, but no details are given of the method or its cost.

LEONTOWITSCH, W. See abs. 1572.

LEPERSON, M. See abs. 2889.

LEPETIT, G. See abs. 3052, 3053.

LERNER-STEINBERG, B. See abs. 3579.

2094. LE ROSEN, A. L., AND OWENS, M. L. Method for the Estimation of Oxy Compounds, Aromatic Hydrocarbons, and Nonaromatic Hydrocarbons in Certain Petroleum Products. Am. Chem. Soc., 117th Meeting Abs., March–April 1950, B, p. 1.

Rapid chromatographic method is proposed for the analysis of various hydrocarbon synthesis products in terms of the following classes of compounds: Oxygen-containing compounds, aromatic hydrocarbons, and nonaromatic hydrocarbons. A sample volume of 0.5 ml. is required, and the time consumed in an analysis is less than 1 hr.

LESSING, R. See abs. 1287.

2094a. LE THOMAS, A. AND MORLET, E. [Slow Graphitization at Moderate Temperatures.] Bull. assoc.

tech. founderie, No. 9, 1932, Suppl. 20–22; Chem. Abs., vol. 27, 1933, p. 691.

Prolonged dilatometric tests were made on Fe containing total C 3.5, Si 1.57, Mn 0.71, S 0.10, P 0.56%. Examination of the structure and mechanical testing shows that this Fe is susceptible to graphitization at 450° after it is maintained for 700 hr. at this temperature, while its properties were noticeably changed. However, a dilatometric test made in the usual way for a short time at temperatures <690° did not modify the sample.

2095. LEVA, M. Heat Transfer to Gases Flowing in Turbulent Motion Through Packed Tubes. Ind. Eng. Chem., vol. 39, 1947, pp. 857–862; Chem. Abs., vol. 41, 1947, p. 4972.

This has been investigated for Reynolds numbers larger than 200. From the data obtained a dimensionally sound equation is developed, which holds very well for pipe diameters ranging from 0.622–3.1 in. Heat-transfer coefficients were measured for air, CO₂, and N₂, and the equation holds true in all cases very satisfactorily. h (film heat transfer coefficient) was differentiated with respect to D_p at D_t (packing diameter at tube diameter) = constant, and a maximum coefficient was predicted and experimentally verified for D_p/D_t = 0.150. The effect of the Prandtl group upon h is discussed in detail. The effect of voids upon h was studied. It was found that no coordinated relationship between h and voids existed.

2096. ——. Elutriation of Fines From Fluidized Systems. Chem. Eng. Progress, vol. 47, 1951, pp. 39–45.

Some fundamental relationships between operating variables and elutriation from fluidized systems are discussed. Special attention is given to fluidized beds, such as Fischer-Tropsch catalysts. The simplest type of systems was investigated, those essentially composed of one coarse and one fines component. Rates of elutriation could be expressed by way of the law governing 1st-order chemical reactions and typical rate constants could be calculated. It was shown that the rate constants are related to such variables as linear gas velocity, size of coarse and fines constituents, material density, and bed height. The gas velocity was recognized as a system driving force, and an analogy was suggested between a system of fines in coarse particles or solutions. The analogy was extended further, and it appeared that concentration conditions in dense-phase and dilute-phase fluidized systems could be related by a modified form of Henry's law.

——. See abs. 3090.

2097. LEVA, M., AND CROWELL, J. H. Heat Transfer Through Packed Tubes With Chemical Reaction. Am. Chem. Soc., 111th Meeting Abs., 1947, p. 141.

Reviews previous work in field. Actual experimental temperature distribution data through packed tubes give coefficients that agree with those calculated from equations 1 and 2 for heating and cooling, respectively, and in which the use of the logarithmic mean temperature difference is employed. Heat-transfer data observed with a typical strongly exothermic chemical reaction taking place in the catalytic tube are presented and compared with coefficients estimated by means of the cooling correlation given by equation 2. For the range over which the heat-transfer coefficient correlation was meant to apply—that is, for modified Reynolds numbers lying between 200 and 3,500—the agreement between the observed and calculated values is in the neighborhood of 10%, the calculated coefficients being the lower and more conservative values. This agreement is considered to be close enough for design purposes and for the general overall estimation of the over temperatures in catalytic reactors. Several possible explanations are given why the co-

efficients through the catalytic reactor should be somewhat higher than the values estimated by equation 2. A new concept of average distance of heat travel and a criterion for the efficiency of a tube in the removal of heat are introduced. These may perhaps be useful for consideration of heat flow through tubes of shapes other than those of the conventional circular cross section.

2098. LEVA, M., AND GRUMMER, M. Heat Transfer to Gases Through Packed Tubes—Effect of Particle Characteristics. Ind. Eng. Chem., vol. 40, 1948, pp. 415–419; Chem. Abs., vol. 42, 1948, p. 5281.

2099. LEVA, M., WEINTRAUB, M., AND GRUMMER, M. Heat Transmission Through Fluidized Beds of Fine Particles. Chem. Eng. Progress, vol. 45, No. 9, 1949, pp. 563–572.

Equation is derived for the calculation of heat-transfer coefficients through fluidized beds in terms of characteristic fluidization variables. The study was made in tubes of 2- and 4-in. diameter with round sand, sharp sand, and an Fe Fischer-Tropsch catalyst (Fe₃O₄) in the particle size range of 400–100 mesh. In attempting to correlate the data, 3 equations were developed, the last of which, $h = 0.35 c_p G^{1.15}$, in which h is expressed in B. t. u./hr./sq. ft./F°, C_p in B. t. u./lb./F° and G in lb./sq. ft./hr., represents the data with an accuracy of $+$ or -27.5%. Within the limits of the experimental data, it is shown that the bed height, the concentration of solids in the bed (state of expansion), the density of the solid phase, and the vessel diameter had no effect upon heat transfer. It is concluded also that the tube diameter affects fluidization less than has been believed. Application of the equation to design of reactors utilizing the fluidization technique is discussed. Channeling has a very pronounced effect on heat transfer. Absolute particle size and shape are considerably more important than size distribution in inducing channeling.

2100. LEVA, M., GRUMMER, M., WEINTRAUB, M. AND POLLCHIK, M. Introduction to Fluidization. I. Chem. Eng. Progress, vol. 44, No. 7, 1948, pp. 511–520.

Counterflow and cogravity flow of air, CO₂, and He through beds composed of round and sharp sand have been investigated. Countergravity flow does not differ from cogravity flow as long as no bed expansion is experienced. Correlations have been developed that permit the prediction of the fluid velocity necessary to expand a bed of sand under countergravity flow conditions. Correlations include a shape factor, and typical photographs of the various sizes and shapes of sands are presented to permit comparison of any new materials with those tested. In this way, it is believed the approximate shape factor of new and similar materials may be determined satisfactorily. The equations presented apply also to mixed sizes of sands, provided the effective diameter of the mixture is evaluated, according to the rule suggested. The most-complex mixture investigated was composed of 5 individual components. It is believed that the correlations apply also with good results to more-complex mixtures. Describes typical fluidization phenomena in 2.5- and 4-in. tubes.

2101. ——. Fluidization of Solid Nonvesicular Particles. II. Chem. Eng. Progress, vol. 44, No. 8, 1948, pp. 619–626; Chem. Abs., vol. 42, 1948, p. 7583.

Fundamental correlations for the fluidization of small particles are developed from experimental data. The experimental work was carried out with round and sharp silica sands varying in size from 0.01505–0.00202-in. effective diameter. The flow of air, CO₂, and He through beds of these particles in a 2.5-in. and 4-in. tube was investigated. A distinction is made between expanded and fluidized beds. It was found

that a bed of fine particles must have a certain minimum voidage before fluidization sets in. This minimum fluid voidage has been correlated with the effective diameter of the bed particles for the various shapes considered. With the minimum fluid voidage available and the pressure-drop law describing flow of fluids through packed beds, the onset of fluidization may be predicted. Interpretation of the data permitted the definition of a fluidization efficiency, which may perhaps be used as a criterion for the quality of fluidization operations. Correlations have been applied with good results to mixed sizes up to 5 individual components. The slugging behavior of fluidized beds was considered, and an attempt was made to correlate slugging points. 2 typical problems illustrate the applications of the new correlations; 1 demonstrates that the correlations are also valid for the upward flow of liquids through beds of fine particles.

2102. LEVA, M., GRUMMER, M., WEINTRAUB, M., AND STORCH, H. H. Study of Fluidization of an Iron Fischer-Tropsch Catalyst. III. Chem. Eng. Progress, vol. 44, No. 9, 1948, pp. 707–716; Chem. Abs., vol. 42, 1948, p. 7957.

Earlier fluidization correlations, based on experimental work with silica-sand beds, are briefly reviewed. New data, observed during the fluidization of a typical fused-Fe Fischer-Tropsch catalyst, are presented This material was considerably more irregular than sharp sand. Typical mixtures, comprising components varying in size from 32–325 mesh, were investigated by using air and He as fluids. It appeared that the new data agreed with the correlations based on the experimental work with sand beds when proper allowance was made for the greater irregularity of the particles. The application of the correlations to process design is discussed on the basis of typical Fischer-Tropsch operating data. The importance of correct evaluation of the physical properties of the reaction mixture was stressed in the application of the correlations. In connection with process calculations, a simple semigraphic method for solving problems was proposed.

2103. LEVA, M., WEINTRAUB, M., GRUMMER, M., AND CLARK, E. L. Cooling of Gases Flowing in Turbulent Motion Through Packed Tubes. Ind. Eng. Chem., vol. 40, 1948, pp. 747–752; Chem. Abs., vol. 42, 1948, p. 5277.

Heat-transfer coefficients were determined for the flow of heat from hot air and CO₂ to cooling water. Tests were made with a 2-in. and a ¾-in. standard packed tube. The packing material was of low thermal conductivity, spherical, and smooth. The ratio $D_p : D_t$ varied from about 0.08–0.27. The gas-flow range was characterized by the modified Reynold's number interval 250–3,000. 2 dimensionally homogeneous equations were proposed correlating h (heat-transfer coefficient) and the physical properties of the system. The coefficient of the 1st equation was differentiated with respect to D_p at D_t (packing diameter at tube diameter) and G=constant, and a maximum heat transfer coefficient was predicted for $D_p : D_t = 0.153$ and verified experimentally. The heat-transfer coefficient was determined for CO₂ and correlated with that for air; the check between the two was excellent. The possible inclusion of the Prandtl number is discussed as well as the application of the equations to tube sizes larger than 2 in.

2103a. LEVA, M., WEINTRAUB, M., GRUMMER, M., POLLCHIK, M., AND STORCH, H. H. Fluid Flow Through Packed and Fluidized Systems. Bureau of Mines Bull. 504, 1951, 149 pp.

Correlations were developed that would be suitable for the design of equipment in which fluids are brought into contact with granular materials as in the Fischer-Tropsch process.

2104. LEVESQUE, C. L. Oxo Reactions in Industry. Chem. Eng. News, vol. 28, 1950, No. 45, p. 3881.

Paper presented at the October meeting of the Philadelphia and Wilmington Organic Chemists Clubs. The industrial use of certain Oxo reactions and their mechanism were discussed. Certain rules for the addition of CO and H₂ to unsubstituted olefins were presented: (1) Isomerization of the double bond, if possible, generally accompanies the hydroformylation; (2) straight-chain olefins give 40–60% straight-chain aldehydes, and 60–40% of other isomers, the α-methyl one predominating; (3) addition of an aldehyde group to a tertiary C does not occur, no quaternary C atom is found; (4) addition of an aldehyde group adjacent to a tertiary C atom is strongly hindered, but may occur to a small extent; (5) the tertiary C atom does not hinder seriously if the double bond is in the 1, 2-position; (6) addition of the aldehyde group adjacent to a quaternary C does not occur. Several examples are given of reactions that have been run, together with products and yields obtained. The mechanism of the Oxo reduction is believed to center around Co carbonyl or Co carbonium hydride as the actual catalyst. The reaction mechanism must explain the fact that the formyl group always goes on the least substituted C atom, and, except in the case of styrene, the formyl group always appears on the β carbon of an α, β-unsaturated compound.

2105. ——. Oxo Reaction. Chem. Eng. News, vol. 29, 1951, p. 1830.

Paper presented at the National Capital Section meeting of the American Institute of Chemical Engineers. The Oxo reaction shows important possibilities for the production of long-chain alcohols for use in detergents, synthetic lubricants, and plasticizers. It is also of great value as a method for synthesizing aldehydes. The method has been principally used in the United States to synthesize alcohols from petroleum hydrocarbons by hydrogenation of the aldehyde formed in the initial reaction. Standard Oil Co. of New Jersey is operating a plant to produce isooctyl alcohol from a mixture of heptenes. It is reported that Standard Oil Co. of Indiana will erect an Oxo plant soon. The Rohm and Haas Co. is operating a pilot plant to produce several derivatives of 3,5,5-trimethylhexaldehyde from diisobutylene. Use of the Oxo reaction to produce C₅ alcohols has already helped materially to relieve the shortage of 2-ethylhexanol, a prime raw material for the production of plasticizers.

—— *See* abs. 3670.

2106. LEVI, M. G., PADOVANI, C., AND BUSI, M. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen at Ordinary Pressure.] Atti cong. nazl. chim. pura applicata, 3d Cong., 1930, pp. 718–729; Studi ric. comb., vol. 2, 1927–1929, p. 213; Chem. Zentralb., 1931, I, p. 3632; Chem. Abs., vol. 25, 1931, p. 3309.

Experiments were carried out with a carefully prepared mixture of H₂ and CO under well-controlled conditions. Following Fischer's suggestions (abs. 950 and 1021), mixed catalysts were used such as Fe, Co with oxides of Mn or Cr. The yields of liquid hydrocarbon obtained at 257°–285° are of the order of magnitude of those reported by Fischer. The predominant formation of low-boiling hydrocarbons is emphasized. No solid products and comparatively small quantities of gaseous hydrocarbons are formed. The catalysts become less active if reused in several consecutive runs. If the unreacted gas mixture of previous experiments is used for a new run, only liquid hydrocarbons are formed.

LEVIN, H. *See* abs. 3392.

LEVINE, R. *See* abs. 3652, 3653.

2107. LEWIS, W. K. Replaceability of Natural Gas. Gas Age, vol. 98, No. 5, 1946, pp. 29–30; 62, 64.

Emphasizes significance of the possibility of generating both gas and oil from coal by synthetic means. The complete replaceability of natural gas by synthesis gas at a cost that might easily be brought below the delivered cost of natural gas in many areas of the country is thought to be perfectly feasible. It is the opinion that it is not unreasonable to look for considerable commercial development of these synthesis processes within the next 10 yr. The production of synthetic natural gas from coal by the Bergius and Fischer-Tropsch processes is in no sense economically out of the question in the not distant future.

2108. ——. Kinetics of the Reactions of Steam and Carbon Dioxide With Carbon. Chem. and Eng. News, vol. 25, No. 39, 1947, pp. 2815–2818.

New fluidized powder technique for the efficient combustion and gasification of coal is described in the Priestley medal address. In this method, finely powdered coal, actually suspended by a stream of air entering at the bottom of the retort, is subjected to air and steam and converted into a mixture of CO and H₂ gases. Combining with O₂ in the air, CO₂ is formed, and heat is evolved. In the upper part of the retort the CO₂ and heat encounter more C, in the form of powdered coal and steam. 3 important reactions then take place, during which heat is absorbed, while the CO₂ is transformed into CO and H₂. Rapid and even heat distribution is the basis for the success of the method, compared with the older processes in which heat is difficult to control. A great advantage of fluidized powder technique is that all grades of coal can be used. Other advantages are the reduction of operating difficulties owing to elimination of excessive temperatures; prevention of slag formation; reduction of unburned fuel in the refuse and in handling both the coal fed and the ash removed by the fluidized powder technique; high conversion with low CO₂ and undecomposed steam in the product; a definite, though limited, improvement in thermal efficiency; and the reduction in tar formation and its complete utilization. The most serious limitation of the operation is its relatively low capacity; this limit is set by the gas velocity, which cannot be allowed to rise to levels above those necessary for good fluidization. Fluctuations in the gas velocity must also be kept to a minimum. One of its first uses probably will be in the manufacturing of better and cheaper producer gas for industrial purposes. The production of synthesis gas for the Fischer-Tropsch reaction will also be carried out by some modification of this method. The same applies to the synthesis of combustion gases of high heating value.

—— *See* abs. 1097.

2109. LEWIS, W. K. AND FROLICH, P. K. Synthesis of Methanol From Carbon Monoxide and Hydrogen. Ind. Eng. Chem., vol. 20, 1928, pp. 285–290; Chem. Abs., vol. 22, 1928, p. 1324.

Study has been made of some of the factors governing the synthesis of MeOH from CO and H₂ under high pressure and in the presence of a catalyst. MeOH of high purity may readily be prepared by passing a mixture of CO and H₂, preferably at a pressure of several hundred atm. and at temperatures of 300°–350°, over a catalyst composed of metallic oxides. Working with a catalyst of medium activity prepared from the oxides of Cu, Zn, and Al, it is possible to reach nearly theoretical conversion depending upon the pressure, temperature and rate of gas flow employed. CO₂, H₂O and CH₄ may form, but the amount of CO consumed in these side reactions is small under the conditions most favorable to MeOH formation. The catalyst in question appears to be most active at lower temperature and suffers a permanent decrease in activity when exposed to higher temperatures. Also the catalyst is sensitive to poisons.