38, 1942, pp. 363–365; Chem. Abs., vol. 37, 1943, p. 6442.

Virtually no resin formation occurs when gasoline obtained by the Fischer-Tropsch synthesis process is stored, and the mono-olefin content (30–40%) remains unchanged. In general, peroxides are not formed during prolonged storage of large batches of gasoline. Signs of peroxidation have been observed with small batches, for example, the octane number of a sample stored for 15 months in a sealed can was lowerd by 3 units. *o*–Cresol is recommended as a peroxide inhibitor. Samples when tested for knock rating after being taken from a refrigerator gave an octane number 1 unit higher than when tested at room temperature.

662. ———. [Notes on the Examination of Synthetic Benzine.] Oel u. Kohle Erdoel Teer, vol. 39, 1943, pp. 903–910: Chem. Zentralb., 1944, I, p. 199; Chem. Abs., vol. 38, 1944, p. 6066.

Evaporation losses in synthetic benzine amounting to a loss of weight of 2% and a reduction in the Reid pressure of 0.04, caused a fall in octane number. Peroxide formation during storage from the effect of daylight or ultraviolet rays also affected the octane number considerably. The tendency of different synthetic benzines to form peroxide varies. Other factors than the above 2 mentioned also caused changes in the octane number, but the author was unable to determine them.

663. DANULAT, F. [Gasification of Solid Fuels by Oxygen Under Pressure.] Mitt. Metallges., No. 13, 1938, pp. 14–22: Ind. Eng. Chem., news ed., vol. 16, 1938, p. 535; Braunkohle, vol. 37, 1937, pp. 200–202; Chem. Abs., vol. 33, 1939, p. 1471.

Description of commercial manufacture of city gas in Germany by the gasification of brown coal in a plant having two generators of 3.9 ft. diameter, 47,300 lb. of coal is gasified per 24 hr., yielding 563,000 cu. ft. of gas (at 0° and 760 mm.). It is claimed that any noncoking solid fuel can be used for gasification. O_2 is introduced at approximately 300 p. s. i.; this pressure is maintained during gasification of coal. Before entering the generator, the O_2 is mixed with superheated steam at 500°. After purification and CO_2 reduction, the gas has the following composition: CO_2, 3.0; illuminants, 0.5; O_2, 0.1; CO, 22.8; H_2, 48.7; CH_4, 22.6; N_2, etc., 2.3%. For certain synthetic purposes, it is possible to limit the CO production to 15% and increase H_2 to as much as 75% by suitable control of steam input, temperature, and pressure and by use of proper fuels.

664. ———. [Pressure Gasification of Solid Fuels With Oxygen.] TOM Reel 195, pt. 8, item 5 (*see* items 3 and 4); Gas- u. Wasserfach, vol. 84, 1941, pp. 549–552; Chem. Abs., vol. 36, 1942, p. 4315.

Concise description of total pressure gasification of solid fuel by means of pure O_2 and superheated steam. The advantages of this method over previous processes are presented. The operation takes place under a pressure of 20–30 atm., with extensive formation of CH_4, which renders the process so exothermic that consumption of O_2 is greatly reduced. The throughput is increased 5-fold over previous methods because of the reduced amount of gas necessary. Gives some results of pressure gasification of various fuels and includes flowsheets and diagrams of plant with operating data.

DAS, P. P. *See* abs. 166a.

DAUR, R. *See* abs. 1110.

665. DAVEY, W. Synthetic Lubricants. Sci. Lubrication, vol. 2, No. 6, 1950, pp. 10–13; Fuel Abs., vol. 8, No. 6, 1950, abs. 4595.

Polymers of high viscosity index may be prepared by polymerizing C_2H_4, C_3H_6, and C_4H_8 or olefins having more than 8 C atoms in the chain. One process involves cracking a straight-chain wax for a short time at high temperatures and polymerizing the resultant high proportion of olefins. The product is largely a steam-cylinder oil. Moderately viscous oils can also be produced by polymerizing olefins from the 150°–200° Fischer-Tropsch fraction from water gas. A German process uses the chlorination of a Fischer-Tropsch middle oil to give a 20–25% Cl content and reaction of this product with about half its weight of naphthalene in the presence of naphtha and an $AlCl_3$ catalyst. The product yields spindle and turbine oils and a residue of cylinder stock. CO and H_2 may be added to olefins to give aldehydes, which can be reduced to alcohols and oxidized to acids. The esters obtained by combining the long-chain alcohols and acids have high viscosity index and low pour point.

DAVIDSOHN, A. *See* abs. 666.

666. DAVIDSOHN, J., AND DAVIDSOHN, A. Fatty Acids for the Soap Industry. Soap. Sanit. Chemicals, vol. 15, No. 8, 1939, pp. 21–23, 70; Chem. Abs., vol. 33, 1939, p. 8047.

Oxidation of fatty acids and use of products in soap making are discussed. Some mention is made of production of fatty acids by Fischer-Tropsch process.

DAVIDSON, R. L. *See* abs. 1100

667. DAVIES, V. Treatment of Liquid Products From Water-Gas Synthesis. Ind. Chemist, vol. 13, 1937, pp. 442–446; Chem. Abs., vol. 32, 1938, p. 1072.

True vapor-phase process was used to crack Fischer synthetic oil. High pressures are not required, and there is no coke formation. High yields of good-quality motor spirit and 5% residue are produced. Gives flow sheets and photographs of plant.

668. DAVIN, E. [Practical Test of Synthol.] Mat. grasses., vol. 17, 1925, p. 7267; Chem. Abs., vol. 19, 1925, p. 3155.

Crude synthol rectified to 200° gave 87% of distillate suitable as light fuel having d_{20}, 0.8289%; C, 69.29%; H_2, 12.25%, calorific value, 8,200 cal./kg.; the cold test begins to set at —30° and is completely solidified at —90°. Road tests with a 4-hp. motorcycle having a carburetor adjusted for C_6H_6 and running at 25 km./hr. showed the following distances/100 cm.³ of fuel: C_6H_6, 2.9 km.; synthol 3; 1:1 C_2H_6–synthol 3.2, 1:1:1 C_6H_6–alcohol-synthol 2.9. With synthol alone the motor knocks, but with synthol–C_6H_6 it runs quite smoothly.

DAVIS, H. S. *See* abs. 2816.

DAVIS, J. D. *See* abs. 625, 3159, 3213.

669. DAVIS, R. T., JR., DEWITT, T. W., AND EMMETT, P. H. Adsorption of Gases on Surfaces of Powders and Metal Foils. Jour. Phys. and Colloid Chem., vol. 51, 1947, pp. 1232–1248; Chem. Abs., vol. 42, 1948, p. 1102.

Adsorption isotherms for N_2, Kr, n–C_4H_{10}, 1–C_4H_8, and $CHCl_2F$ were measured at temperatures at or below their boiling points and found to be S-shaped on Ag foil, monel ribbon, glass spheres, W powder, ZnO pigments, Al_2O_3, and SiO_2 gel. Cross-sectional areas that had to be assigned to the various adsorbates to bring the calculated surface areas for the last 5 of these adsorbents into agreement with those obtained from adsorption isotherms for N_2 by assigning an area of 16.2 Å.² to the N_2 molecule were: Kr, 20.8 Å.² at —195°; C_4H_{10}, 43.4 Å.² at —78° and 46.9 Å² at 0°; $CHCl_2F$, 37.5 Å.² at —78° and 40.1 Å.² at 0°; and 1–C_4H_8, 42.7 Å.² at 0°. For Ag foil and monel ribbon, these same molecule area assignments yielded absolute areas that were 10% to 60% larger than the geometric surface area when $CHCl_2F$, n–C_4H_{10}, and Kr were used as adsorbates. With molecule area, assignments calculated for these 3 adsorbates from liquid density in the usual way (abs. 827) the surface areas of the Ag foil and monel ribbon obtained from Kr, C_4H_{10}, and $CHCl_2F$ were smaller than the geometric area by as much as 25%.

670. DAVIS, S. G. Evaluation of Catalysts Used in the Synthesis of Hydrocarbons. Canadian Chem. Process Ind., vol. 31, 1947, p. 644.

Abstract of a paper presented at the 3d annual meeting of the Chemical Institute of Canada. A preliminary report is made indicating a method and the apparatus used in the evaluation of catalysts for the reaction of CO and H_2. The apparatus consists of 6 semi-pilot-scale catalyst-testing units. Shows some typical results. Also describes apparatus on which the surface area, the rate of carbiding with CO, and the rate of reduction of the carbide with H_2, are measured on the catalysts.

———. *See* abs. 3747.

671. DAZELEY, G. H., AND GALL, D. Lubricating Oils From Fischer-Tropsch Olefins Using Water Gas as Raw Material. Petroleum (London), vol. 9, 1946, pp. 208–210; Chem. Abs., vol. 41, 1947, p. 2562.

Products obtained by the Fischer-Tropsch process using water gas ($CO:H_2=1:1$) have a considerably higher olefin content than products of similar boiling range obtained from synthesis gas ($CO:H_2=1:2$) and are therefore more promising raw materials for polymerization to lubricating oils. The aim of this investigation was to examine the effects of chain length of olefins and of reaction temperature on the properties of the resulting lubricating oils and on the yields obtained. For a given chain length of olefins, the absolute viscosity of the lubricating oil decreases with increase of reaction temperature, but the V. I. remains approximately constant. Under given temperature conditions, the absolute viscosity of the oil decreases with increase in the chain length of the hydrocarbons in the starting material. The V. I. of all oils prepared from a higher-boiling fraction of gasoline are greater than those of oils from a lower-boiling fraction. The yield of oil calculated on the weight of starting material is less for the higher-boiling gasolines. Calculated on the weight of olefins present, the yield appears to increase with increase in chain length of the hydrocarbons. A marked decrease in yield occurs where a high reaction temperature is employed, but otherwise the effect of reaction temperature on yield is not significant. Reaction temperature and chain length have very little effect on stability to oxidation. The oils are superior in general properties to those obtained from synthesis gas. The V. I. is higher and the oxidation numbers are lower (2.4–2.9, but still too high to comply with Government specification, which requires one below 2). If oils of moderate viscosity and good viscosity-temperature properties are required, it would seem that the most suitable ones are obtained by polymerizing the olefins in the fraction of water-gas gasoline boiling 140°–200°, although the yield is somewhat less than with lower-boiling fractions.

672. DAZELEY, G. H., AND HALL, C. C. Polymerization to Lubricating Oils of 1–Heptene and 1–Pentadecene. Jour. Soc. Chem. Ind., vol. 67, 1948, pp. 22–23; Chem. Abs., vol. 42, 1948, p. 4738.

1–Heptene and 1–pentadecene obtained by synthesis from allyl bromide and the appropriate Grignard reagents were each polymerized with 3–5% $AlCl_3$ at 0°–20° without diluent and also at 80° in a solution in the related paraffin. No sludge formed in the low-temperature polymerization, and the polymerizates had slightly higher viscosity indexes. This suggests that some isomerization occurred at the higher temperature. The yields of lubricating oil were 73–93%. All oils had viscosity indexes in the range 108–132. The oxidation stabilities were independent of the chain length of the original olefin and were significantly better than for the polymerizates from cracked Fischer-Tropsch diesel oil previously described (abs. 673).

673. ———. Preparation of Lubricating Oils From Hydrocarbon-Synthesis Products. I. II. Petroleum (London), vol. 11, 1948, pp. 14–15, 26, 41–44; Chem. Abs., vol. 42, 1948, p. 3943.

Fischer-Tropsch diesel oil may be cracked to yield products containing olefins. Material obtained by thermal cracking at 600° and atmospheric pressure polymerizes in the presence of 5% $AlCl_3$ to give good yields of satisfactory lubricating oil. The products derived from cracking in an autoclave at 450° and over an Al-Si catalyst at 600° give poor yields of lubricating oil on polymerization. The differences in the products are said to be due to the presence of mainly straight-chain α-mono-olefins in the thermally cracked gasolines but not in those formed by other methods of cracking.

674. ———. Production of Olefins by the Cracking of Fischer-Tropsch Waxes and Their Conversion Into Lubricating Oils. Fuel, vol. 27, No. 2, 1948, pp. 50–55; Chem. Abs., vol. 42, 1948, p. 7515.

Total waxes, boiling above 300° at 760 mm., produced at atmospheric pressure and at 10 atm. pressure by synthesis from CO and H_2 in the presence of a Co catalyst were subjected to noncatalytic, vapor-phase cracking at temperatures ranging from 500°–640° and at a throughput of 50 gm. wax per 40 ml. of cracking space/hr. It was found that substantial amounts of α olefins of fairly high purity can be readily recovered from the cracked products. For example, 54 gm. of material, boiling 85°–105°, gave on distillation 36 gm. of n-heptene-1. At a given temperature, the total yield of cracked products is less than for the diesel-oil fraction (200°–300°), but the yield of liquid products is higher. In the range C_5–C_{12} the liquid products from wax contain about 95% of olefins, mainly of the straight-chain α type. The yields and composition of the liquid- and gaseous-cracked products are virtually the same for both waxes. Approximate C-number and olefin-distribution curves for the total products of cracking have been constructed. Polymerization of the olefins with 2–3% of $AlCl_3$ at 80° gives greater yields of lubricating oil with a high viscosity index than are obtained from the products of cracking the diesel-oil fraction, owing to the greater production of long-chain olefins from the waxes. All the oils obtained had B. A. M. oxidation numbers above 2.0.

675. DAZELEY, G. H., GALL, D., AND HALL, C. C. Production of Olefin-Polymer Lubricating Oils of Satisfactory Oxidation Stability. Jour. Inst. Petrol., vol. 34, 1948, pp. 647–653.

Attempts have been made to increase the oxidation stability (as measured by the B. A. M. oxidation-number test) of olefin-polymer lubricating oils derived from the products of the Fischer-Tropsch synthesis. A controlled hydrogenation of the oils in the presence of MoS_2 at 200° and 200 atm. pressure yields an oil with an oxidation number of 1.8. The effect is the result of saturation by H_2 coupled with the formation of S-containing inhibitors and can be accurately reproduced by hydrogenation in the presence of Ni catalyst followed by heating with MoS_2 in the absence of H_2. Treatment of the oil with $AlCl_3$ at 180° produces some improvement in oxidation stability, but the effect is small and is accompanied by a serious loss of oil. Naphthalene added to the olefins before polymerization is chemically incorporated in the resulting oil and leads to an increase in oxidation stability, an increased conversion of the olefins to lubricating oil, and a decrease in the viscosity index of the oil. About 15% napthalene is required to produce an oil with an oxidation number below 2.0; this causes a fall in viscosity index from 100 to a value in the range 80–85.

676. Dean, R. S. Colloidal Behavior in Metals and Alloys. Colloid Chem., vol. 6, 1946, pp. 561–578; Chem. Abs., vol. 40, 1946, p. 2427.

I. Gasses in metals: Physicochemical nature of metallic interfaces; gas-metal systems as colloids; degasification of metals; grain-size control; H. embrittlement. II. Slag-metal systems: Aston wrought-iron process; steel-making reactions; powder metallurgy; magnetic, electric and mechanical properties of metal compacts. III. Dispersions of metals in metals: Solid metals in solid metals; ordering in alloys; dispersion hardening; internal friction or vibration-damping capacity of metals. 78 refs.

677. De Bruijn, H., Westrik, R., and van Loon, W. Dutch Report on Visit to I. G. Farbenindustrie, A.-G., Ludwigshafen and Oppau and Raschig Werke Mundesheim BIOS Miscell. Rept. 104, no date, 126 pp.; PB 96,352.

Some of the subjects reported are: I. Conversion of CO at 25 atm. pressure, the catalyst Fe_2O_3–Cr_2O_3–Na_2SO_4; conversion of CH_4, catalyst Ni on magnesite. II. Conversion of CH_4 to synthesis gas for CH_3OH. III. Synthesis of CH_3OH, procedure, converter, catalyst, temperature, coke-oven gas—the raw material. IV. Manufacture of formaldehyde from CH_3OH. V. Preparation of C_2H_2 from CH_4 by partial combustion and from CaC_2. VI. Preparation of C_2H_4 from C_2H_6 by partial oxidation and by dehydrogenation. VII. Synthetic phenol by Raschig process.

Decarrière, E. *See* abs. 62.

678. Decarrière, E., and Antheaume, J. [An Iron Catalyst for Hydrogenation of Carbon Dioxide at Ordinary Pressures.] Compt. rend., vol. 196, 1933, pp. 1889–1891; Chem. Abs., vol. 27, 1933, p. 4632.

Catalyst containing less Cu than that of Fischer is more active than his original composition. Omission of Cu entirely, however, lowers the activity almost to zero.

Dechamps, G. *See* abs. 2541.

deGodon, F. *See* abs. 2161.

679. de Hemptinne, A. [Synthesis of Organic Compounds by Means of the Dark Electric Discharge.] Bull. Acad. roy. Belg. (3), vol. 34, pp. 269–277; Jour. Chem. Soc., vol 1, 1898, p. 461; Chem. Zentralb., 1897, II, p. 1044.

When mixtures of CO and H_2 are subjected to the silent electric discharge, CH_2O and its polymers are produced. CO and CH_4 yield an aldehydic substance and CO and C_2H_6 form a ketone and an aldehyde.

680. Delaunay, R. [Methanol Synthesis From Wood by the Lacotte Process.] Chim. et ind., vol. 58, No. 4, October 1947, pp. 335–340; Chem. Abs., vol. 42, 1948, p. 1041.

Describes first plant-scale operation of the Lacotte process for the manufacture of synthetic MeOH from wood. The particular originality of the process, as carried out at the Decazeville plant, lies in the Lacotte gas producer, which directly and continuously produces synthesis gas of such high purity that its purification is unnecessary before use. The catalytic synthesis of MeOH utilizes as a catalyst a mixture of the oxides Zn and Cr deposited on a carrier. The operation takes place at a temperature of 425° and a pressure of 650 kg./cm.^{2} The plant processes 20 tons of wood of 25% water content/day and produces 6,000 l. of MeOH of 99.9% purity. Each l. of MeOH requires 2.7 m.^{3} of synthesis gas, 3.3 kg. of wood of 20–25% moisture, 0.8 m.^{3} of 98% O_2, 2.8 kw.-hr. of electricity, and 0.7 kg. of steam. 1 ton of dry wood gives 3 hl. of MeOH.

Delion, R. *See* abs. 1604.

Delle, V. A. *See* abs. 2431.

681. Delley, E. [Substitute and Synthetic Motor Fuels.] Schweiz. Techztg., 1938, pp. 59–66, 75–80; Chem. Zentralb., 1938, II, p. 234; Chem. Abs., vol. 34, 1940, p. 3469.

Exhaustive report of methods of production, possibilities for use, and production figures for the hydrogenation products of coal (Bergius-I. G. and Fischer-Tropsch processes) and C_2H_2; for EtOH and MeOH, benzene, and vegetable oils; for the products of distillation of asphalt and bituminous shales; for gaseous fuels such as compressed city gas from sludge digestion, coke-oven gas and CH_4, C_2H_2, NH_3, and H_2; and for gaseous fuels such as coal gas. Discusses their utilization in Switzerland.

682. Demann, W. [Semicoke for Chemical and Metallurgical Processes.] Glückauf, vol. 73, 1937, pp. 1101–1106; Coal Carbonisation, vol. 4, 1938, p. 16.

A general survey of the use of semicoke is followed by notes on the results of various large-scale trials, including the manufacture of synthesis gas by the Ruhrbenzin A.-G.; the direct manufacture of synthesis gas in water gas producers at the Grasbrook (Hamburg) gas works; and the manufacture of ferrosilicon, CaC_2, and other products.

683. ———. [Status of Low-Temperature Coking in Germany and Its Relation to the German Power Situation.] Gas- u. Wasserfach, vol. 85, 1942, pp. 375–381; Chem. Abs., vol. 37, 1943, p. 4551.

Review of low-temperature coking processes, with 52 refs. Tar obtained by low-temperature coking of bituminous coal differs from that obtained from brown coal by its aromatic-naphthenic structure; gasoline obtained from this tar has an octane number of 80–90. Coke from low-temperature carbonization of bituminous coal of an ash content of 2% or less is used for metallurgical purposes, for example, the manufacture of ferrosilicon. To obtain tars suited for the manufacture of motor fuels several German gas works have installed special coking apparatus in their gas generators. The Müller process (abs. 2337), which combines low-temperature coking with the Fischer-Tropsch hydrocarbon synthesis increases the oil yield of the synthetic process by 20–30%.

684. den Otter, H. P. [Mersol and Sodium Mersolsulfonic Acid.] Chem. Weekblad, vol. 43, 1947, pp. 211–217, 276–282; Chem. Abs., vol. 41, 1947, p. 5327.

Describes manufacture of Mersol by reaction of SO_2 and Cl with hydrocarbons produced by the Fischer-Tropsch synthesis. Depending upon the reaction conditions, this produces Mersol D (50–60% of monosulfonyl chloride, 10–20% of di- and higher sulfonyl chlorides, and about 20% of unchanged hydrocarbon) or Mersol H_2 (about 50% monosulfonyl chloride and 50% of unchanged hydrocarbon). Unchanged hydrocarbon is best removed by extraction with benzine; steam distillation is too expensive. Production of Mersolat and its use as a detergent are described.

685. ———. [Soap From Synthetic Fat Acids. I.] Chem. Weekblad, vol. 43, 1947, pp. 37–42.

Review and discussion of the literature, with 76 refs.

686. ———. [Soap From Synthetic Fat Acids. II.] Chem. Weekblad, vol. 43, 1947, pp. 120–122, 131–134; Chem. Abs., vol. 41, 1947, p. 3310.

Review and discussion of the literature, with 153 refs.

687. ———. [Soap From Synthetic Fat Acids. III] Chem. Weekblad, vol. 43, 1947, pp. 740–747; Chem. Abs., vol. 43, 1949, p. 7241.

Review and discussion of the literature, with 105 refs.

688. ———. [Soap From Synthetic Fat Acids. IV.] Chem. Weekblad, vol. 43, 1947, pp. 740–747; Chem. Abs., vol. 42, 1948, p. 1439.

Sample of synthetic fat acids as used in Germany in 1943–1944 was found to have a composition approximately similar to that of a mixture of 50% coconut-oil-fat acids and 50% lard-fat acids but to contain little oleic acid. On preparation of the Na soap-fat acid, losses of 5% were observed. The soap contained 0.71% NaCl. Compared with soaps made from natural-fat acids it lacked plasticity; it suffered greater loss in use; its foam was equal in quantity but less stable; its cleaning power was inferior; and its odor was disagreeable.

689. Dent, F. J. Use of Oxygen for Town-Gas Manufacture. Gas World, vol. 128, 1948, pp. 384–385.

Proposal for pressure gasification of coal linked with a synthetic-oil process for the production of town gas. Data so far available indicate that pressure gasification might assume the basic position in the gas industry that carbonization now occupies provided the demand for gas outstrips that for coke; the process also would have the advantage of flexibility in operation during peak periods. As compared with the Fischer synthesis process, gasification under pressure, with withdrawal of part of the gas for oil synthesis, shows many advantages. Assuming an overall thermal efficiency of about 70%, the gas cost is reduced to 0.65 d. per therm.

———. *See* abs. 2302.

690. Dent, F. J., and Hebden, D. Catalytic Synthesis of Methane as a Method of Enrichment in Town-Gas Manufacture. Gas Research Board Rept. 51; Gas World, vol. 130, 1949, pp. 1938–1939; vol. 131, pp. 69–75.

Experiments were carried out to demonstrate that catalysts can be operated successfully at the high space velocities necessary on gas-production plants by suitably controlling the temperature of the catalyst surface and by using catalysts of suitable composition. Temperature control was maintained by recirculation of the heating gases. Operating with blue water gas at a space velocity of 2,000 vol. per vol. per hr., a final gas of approximately 500 B. t. u. per cu. ft. was made at atmospheric pressure, and with a H_2-rich gas of more than 700 B. t. u. it was made at 20 atm. During a 4-month run with no appreciable deterioration in the calorific value and with a catalyst life of this length, the catalyst cost should be no more than 0.3 d. per therm. There are two possible applications of the synthesis reaction that are worth consideration: As an alternative to oil for enrichment of blue water gas at times when the maximum thermal output of gas is not required from the water gas plant, and for enrichment of gas produced by the gasification of coke breeze at moderate pressure with O_2 and steam. In the first case, the margin between the cost of the raw material and the value of the synthesized product should be enough to cover the installation and operation of the synthesis plant. Determination of the efficiency of the gasification of breeze under pressure and of the outputs obtainable is to be made soon under pilot-plant conditions.

Dent, F. J., Blackburn, W, H., and Millett, H. C. Investigation of the Use of Oxygen and High Pressure in Gasification. II. Synthesis of Gaseous Hydrocarbons at High Pressure. *See* abs. 692.

———. Investigation of the Use of Oxygen and High Pressure in Gasification. III. Synthesis of Gaseous Hydrocarbons at High Pressure. *See* abs. 693.

Dent, F. J., Blackburn, W. H., Millett, H. C., and Moignard, L. S. Investigation of the Use of Oxygen and High Pressure in Gasification. IV. Synthesis of Gaseous Hydrocarbons at High Pressure. *See* abs. 694.

691. Dent, F. J., Blackburn, W. H., Williams, N. H., and Millett, H. C. Investigation of the Use of Oxygen and High Pressure in Gasification. I. Gasification With Oxygen. Rept. 39. Joint Research Committee, Institution of Gas Engineers and University of Leeds; Inst. Gas Eng. Commun. and Repts., Commun. 141. 1936, 76 pp.; Trans. Inst. Gas Eng., vol. 86, 1936–1937, p. 118; Chem. Abs., vol. 31, 1937, p. 7225.

Discusses results for Lurgi plant using lignite. Coke from Sharlston and Warrenhouse coals were studied in a laboratory apparatus described. The Warrenhouse was a more reactive and, therefore, a better product than the Sharlston coke, giving lower outlet temperature, lower O_2 consumption, and less sensible-heat loss, and allowing the use of a lower steam : O_2 ratio. Addition of Na_2CO_3 improved the reactivity of Warrenhouse coke. Preheating of steam and O_2 also gave improved results. Use of air-steam mixtures instead of O_2-steam increased the heat losses. The influence on the results of rate of gasification and size of coke was studied. Gives results for gasification using O_2–N_2 and O_2–CO_2 mixtures. Blowing O_2 instead of air through a heated coke bed reduced CO formation and sensible-heat losses.

692. Dent, F. J., Blackburn, W. H., and Millett, H. C. Investigation of the Use of Oxygen and High Pressure in Gasification. II. Synthesis of Gaseous Hydrocarbons at High Pressure. Rept. 41, Joint Research Committee, Institution of Gas Engineers and University of Leeds; Inst. Gas Eng. Commun. and Repts., Copyright Pub. 167/56. 1937. 58 pp.; Trans. Inst. Gas Eng., vol. 87, 1937–1938, p. 231; Gas Jour., vol. 220, 1938, pp. 470, 473–475, 658–659; Gas World, vol. 107, 1938, pp. 424–425, 545–546; Chem. Abs., vol. 32, 1938, p. 6435.

Preliminary experiments showed that it was possible to gasify all types of bituminous coals and lignite in steam under pressure with synthesis of hydrocarbons in the fuel bed and the production of a gas of calorific value high enough for general supply. Various types of fuels were heated to 800° (1½–2¾ hr.) in a stream of H_2 or gas contg. H_2 at 1–100 atm. pressure and held for 1½ hr.; similar tests in N_2 were run for comparison. Results with a coke prepared at 450°–500° from Yorkshire coal are typical. In N_2, yields at atm. pressure were H_2 23.0; CH_4, 14.7; and total gaseous hydrocarbons 16.3 therms per ton of coke. In H_2, yields at atm. pressure were H_2 1.3 and gaseous hydrocarbons 33.8 therms. At 5 atm., yields of gaseous hydrocarbons were 92.1 therms; at 10 atm., 132.9 therms; at 25 atm., 202.5 therms; at 50 atm., 276.0 therms; and at 100 atm., 311.2 therms. CH_4 still was being formed at the end of the tests. At 50 and 100 atm., tar yields increased. Maximum calorific value of outgoing gas in B. t. u. per cu. ft. was 345 at 1 atm., 429 at 5 atm., 500 at 10 atm., 589 at 25 atm., 719 at 50 atm., and 914 at 100 atm. Calorific value increased with increasing rate of heating or decreasing rate of H_2 supply, although there was an accompanying decrease in yield of hydrocarbons. H_2 absorption, in therms per ton, was 32.9 at 5 atm., 60.8 at 10, 107.7 at 25, 153.5 at 50, and 193.5 at 100. The coke contained 19.8% volatile matter, but % losses in weight were 18.6 at 1 atm., 27.7 at 5, 34.9 at 10, 44.6 at 25, 62.4 at 50, and 72.0 at 100. At low pressure, hydrogenation was most rapid at 500°–550°; at higher pressure, 700°–750°. These are temperatures related to thermal decomposition of coke; hence H_2 merely modifies the course of the decomposition. The thermal yields of gaseous hydrocarbons were not reduced by substitution of

$CO–H_2$ mixtures for H_2 if the rate of supply and pressure were increased to allow for lower H_2 in the mixture; CO dilution reduced the calorific value of gas.

693. ———. Investigation of the Use of Oxygen and High Pressure in Gasification. III. Synthesis of Gaseous Hydrocarbons at High Pressure. Rept. 43, Joint Research Committee, Institution of Gas Engineers and University of Leeds; Inst. Gas Eng., Copyright Pub. 190/73, 69 pp.; Gas Jour., vol. 224, 1938, pp. 442–445, 627–628; Gas World, vol. 109, 1938, pp. 364–365, 401–404; Trans. Inst. Gas Eng., vol. 88, 1938–39, p. 150; Chem. Abs., vol. 33, 1939, pp. 6561–6562.

In a continuous plant, coals and cokes prepared at temperatures up to 800° could be virtually completely gasified in H_2 at 50 atm. if the temperature of the fuel bed were maintained around 900° and if, with coals, caking properties did not occasion difficulties on the larger scale of operation. Rate of gasification was accelerated by alkalies, but the effect was most marked in hydrogenating at low temperatures. A coke prepared from an intimate mixture of coal and 3% Na_2CO_3 gave 463 therms of gaseous hydrocarbons/ton when hydrogenated at 800°, but gave only 140 therms in absence of alkali; at 900° the coke gave 520 therms without alkali, but alkali accelerated the rate toward the end of hydrogenation. Alkali reduces the tendency of coal to cake during treatment. Highest percentages of CH_4 obtained at 50 atm. were 57.3 at 800°, 43 at 900°, and 36.3 at 950°; therefore, gas of 600 B. t. u. cannot be prepared above 915°; of 700 B. t. u., above 810°; of 800 B. t. u., above 700°. If higher temperatures of treatment are necessary to secure proper reactivity of coke, the lower limit of pressure must be increased. Data are also given for H_2 containing CO, CO_2, and N_2. There are 2 periods in the hydrogenation: (1) Thermal decomposition of coal while temperature is raised and (2) thermal stability of the solid residue at a steady temperature. During (2), rate of formation of hydrocarbons was limited and depended on final temperature maintained. During (1), high rates of heating gave high hydrocarbon production. For example, heating at 12°/min. and using 58,000 cu. ft. of H_2/hr./ton produced the first 200 therms at an average rate of 220 therms/hr., corresponding on dilution to gas of 500 B. t. u. with a rate of 415 therms/hr./ton (normal carbonization 7 therms/ton/hr.). Complete gasification of coals in H_2 to simple hydrocarbons involves breaking down 6-membered C rings. With benzene under the above experimental conditions, gaseous hydrocarbons were formed at 750°; at 850°, ⅔ was decomposed to CH_4 in 1 min. Anthracene was more readily decomposed. With xylene, CH_4 formation was appreciable at 550°–600°; hydrogenation of side chains was complete at 700°.

694. Dent, F. J., Blackburn, W. H., Millett, H. C., and Moignard, L. S. Investigations of the Use of Oxygen and High Pressure in Gasification. IV. Synthesis of Gaseous Hydrocarbons at High Pressure. Rept. 50, Joint Research Committee, Institution of Gas Engineers and University of Leeds; Inst. Gas Eng. Commun. and Repts., Commun. 26, 1946, 52 pp.; Gas World, vol. 125, 1946, pp. 680–682; Chem. Abs., vol. 41, 1947, p. 3277.

In the light of the knowledge gained in the laboratory, consideration is given to 4 processes: (1) The Lurgi process for complete gasification; (2) a 2-stage process for complete gasification involving the production of gaseous hydrocarbons by hydrogenation; (3) a process of gasification at high pressure combined with CH_4 formation by catalytic synthesis; and (4) a process of carbonization in which internal heating is obtained by the exothermic hydrogenation and decomposition of the coal. It is doubtful whether the Lurgi process would produce, from British coals, a gas with as high a heating value as that normally supplied, and it would probably require some pretreatment of the fuels to render them noncaking. When complete gasification is required the 2d process is more suitable for bituminous coals. A detailed analysis of the mechanism by which gaseous hydrocarbons are produced indicates that, in this process also, the yield of enriching hydrocarbons would be limited. It appears that gas of approximately 500 B. t. u./cu. ft. might be readily obtained by synthesis without the need of additional gaseous hydrocarbons from hydrogenation. The solid residue from the hydrogenation of coal is particularly combustible; although in the laboratory it had not been obtained as yet in large strong pieces. Coals were hydrogenated in a vessel of 6⅜ in. internal diameter, which was not externally heated. All coals except anthracite fused under high pressure; and, unless they were first rendered noncaking, difficulty was encountered in securing uniform gas flow and reaction throughout the charge. Coals that were not pretreated could be hydrogenated if the sizes below ⅛ in. were separated and charged down the side of the vessel. With such a graded charge it was possible to treat satisfactorily a wide range of coals, including semianthracites, caking coals, and high-volatile, weakly caking coals. When coals were heated under controlled temperature conditions and under pressure in a 1-in.-diameter reaction tube the gas arising from the decomposition of the fuel was high in hydrocarbons, even when the atmosphere supplied was rich in hydrocarbons. At 50 atm. and 800°, gas containing 30% CH_4 was prepared from C and H_2 at space velocities as high as 20,000 with Ni supported on porous pot as the catalyst. CH_4 was decomposed rapidly and almost completely at a high temperature, high pressure, with excess steam, and in the presence of a Ni catalyst.

695. de Pauw, F., and Jungers, J. C. [Kinetics of Hydrogenation of Acetylene on Nickel.] Bull. soc. chim. Belg., vol. 57, 1948, pp. 618–630; Chem. Abs., vol. 44, 1950, p. 915.

Hydrogenation of C_2H_2 (I) to C_2H_4 (II) or C_2H_6 was observed in a static system by means of pressure drops. Catalyst (A) was prepared by reducing $NiCO_3$ precipitated on kieselguhr; (B) was prepared by reducing oxide from the calcination of $Ni(NO_3)_2$ at 350°. With (A) and equimolar H_2 and (I) there was no reaction at 29°–100°, but if H_2 was admitted first, there was rapid reaction. With equimolar H_2 and (II) there was reaction. It was concluded that (I) by forming polymers poisoned the catalyst. Using the less active catalyst (B) tempered by heating in a H_2+(I) mixture at 300°, and an excess of H_2 over (I) (ratios 2–20), it was possible to make kinetic experiments. The catalyst was periodically regenerated with H_2 at 300°. At 29°–30°, an initial reaction of steady rate continued until about 1 mol. of H_2 was used per mol. of (I); the rate then increased. For the initial period, rate $=k(H_2)/(I)^{1/2}$. The reaction was faster for D_2 than for H_2. The activation energy (16°–57°) for (I) hydrogenation was 14 kg.-cal.; for (II) it was 10 kg.-cal. Results are explained by strong adsorption of (I), which inhibits hydrogenation of (II) as long as (I) is present. The rate laws are fitted by means of Langmuir adsorption formulas. The adsorption coefficient of (I) is estimated to be 100 times that of H_2 at 30°, whereas that of D_2 is about 1.5 times that of H_2.

Derrig, M. J. *See* abs. 3599.

696. Dersin, H. [Synthesis of Higher Alcohols From Carbon Monoxide and Hydrogen.] Chem.-tech. Rundschau, vol. 44, 1929, p. 310; Chem. Abs., vol. 23, 1929, p. 3661.

By passing CO and H_2 over the same catalyzers, but at a slower rate than for MeOH, alcohols of higher molecular weight may be obtained. These are contaminated with MeOH, aldehyde, amines, and small quantities of liquid hydrocarbons. By suitable variation in the operating conditions formation of higher alcohols is favored. Patent literature is reviewed.

697. ———. [Synthetic Production of Methanol From Carbon Monoxide and Hydrogen.] Chem.-tech. Rundschau, vol. 44, 1929, pp. 146–148, 176–178; Chem. Abs., vol. 23, 1929, p. 3661.

Review of periodical and patent literature on production and purification of initial materials, apparatus, catalyzers, and purification of the crude methanol.

Desormes, —. *See* abs. 580.

698. Deville, H. S. [Dissociation of Carbon Monoxide.] Compt. rend., vol. 59, 1864, p. 873; vol. 60, 1865, pp. 317–325.

Discovery is made that the reaction $CO_2+C=2CO$ is reversible. Only a small degree of dissociation was observed at temperatures a little lower than the melting point of Ag, while at temperatures above 1,000° none could be observed.

699. Dew, W. A., and Taylor, H. S. Adsorption and Heat of Adsorption of Ammonia Gas on Metallic Catalysts. Jour. Phys. Chem., vol. 31, 1927, pp. 277–290; Chem. Abs., vol. 22, 1928, p. 1074.

Measurements of the specific adsorption and heats of adsorption of NH_3 on Cu, Ni, and Fe catalysts have been made by methods previously used in order to study the reaction: $2NH_3=N_2+3H_2$. Values for the specific adsorption of NH_3 and H_2, and some figures for N_2 on Na, Cu, Ni, and Fe and 50–50 Fe-Mo at 0°, 110°, 218°, 305°, and 444.6°, with a number of exceptions, are given, which show that the catalysts adsorb NH_3, that the adsorption is reversible at low temperatures, and that decomposition occurs at higher temperatures. Differential heats of adsorption for NH_3 at 0° on Cu, Ni, and Fe and integral heats for NH_3 at 0° on Cu and Ni have been given. The beneficial effect of low-temperature preparation of catalysts upon the adsorption effect is stressed, and indication is found that the higher the heat of adsorption the greater the possibility of catalytic activity.

700. Dewar, J., and Jones, H. O. New Iron Carbonyl and the Action of Light and Heat on the Iron Carbonyls. Chem. News, vol. 95, 1907, pp. 97, 109; Chem. Abs., vol. 1, 1907, p. 1226.

701. Dewey, D. R. Hydrocarbon Synthesis. Wartime Work of the Kaiser-Wilhelm Institut für Kohlenforschung. Ind. Chemist, vol. 21, 1945, pp. 681–683; Chim. et ind., vol. 55, 1946, pp. 327–328; CIOS Rept. XXV/27, 1945; U S. Naval Tech. Mission Rept. (in Europe), 110–45; TOM Reel 196; PB 289, 890, L 86,445; Chem. Abs., vol. 40, 1946, p. 7,557.

Supplements the disclosures made by F. Fischer on his retirement as Director in 1943 (abs. 972). Co remains the best catalyst for the normal-pressure synthesis; the Fe catalyst was found to be unsuitable. In the medium-pressure synthesis, use of the Co catalyst gives a low yield of olefins and a high yield of paraffins, whereas the contrary is true with the Fe catalyst. The Fe can be combined with 2–3% Cu and up to 1% of alkali; the higher the proportion of alkali, up to this limit, the higher the average molecular weight of the hydrocarbons made. A pressure of 20 atm. gives the highest factor of conversion and the best yield of high-molecular compounds. Below 10 atm. the life of the catalyst decreases rapidly and above 20 atm. the formation of O-containing compounds begins. The best composition for the synthesis gas is 1 CO : 1H_2. Typical yields with Fe catalyst are as follows: C_3–C_4 compounds containing 50% olefins; 20% gasoline fraction containing 50% olefins; 40% fraction boiling 200°–300°; 20% waxes m. p. above 15° 20%. The temperature for the Co catalyst is about 190°, for the Fe 240°. Evidently Fe was used in the commercial process to save the available Co for the Kogasin synthesis; Fe produces the waxes in satisfactory quantity, and that was the main point regardless of the nature of the lower products and the smaller yield of waxes than with Co. The direct synthesis of iso-compounds dates only from 1940–41 and began with the production of C_3H_8–C_4H_{10} mixtures with up to 90% of iso-C_4H_{10} in the C_4 fraction. It is thought that the formation of iso-compounds arises from the chain of reactions: water gas to higher alcohols; dehydration of alcohols to olefins; hydrogenation of olefins to isoparaffins. Catalysts capable of promoting the simultaneous progress of these reactions include ThO_2, Th and Al oxides, Zn and Al oxides, Al_2O_3, and ZnO with Th, Ce, or Zr oxide. The reaction is best carried out with a gas 1.2 CO : 1 H_2 at 450° and 300 atm. With a ZnO–Al_2O_3 catalyst the composition of the products from C_4 upward is: C_4H_{10} (90% iso-C_4H_{10}), 60–70% by weight; C_5H_{12} (96–98% iso-C_5H_{12}), 20–30% by weight; C_6, C_7, and C_8 small amounts. Up to about 10% of alcohols, mostly isobutyl, is produced also. The proportion of compounds with different numbers of C atoms in the molecule may be varied by altering the composition of the catalyst; if the ZnO is increased the proportion of higher compounds rises, and vice versa. The ZnO–Al_2O_3 catalyst seems to be the best commercial proposition, because of its cheapness, but a catalyst of Al_2O_3 and ThO_2 (4 : 1) gives less alcohol and permits a faster gas rate. Above 300 atm. (the best operating pressure) O-containing compounds are formed in increasing amounts. At 400° the yield includes a high % of alcohols; at a slightly higher temperature dimethyl ether is produced; there is quite a narrow band around 450° where iso-C_4H_{10} is produced; above this temperature the deposition of C becomes excessive. The synthesis is generally insensitive to S. Catalysts are known to be good for 6 months without any decrease in activity. With the Ru catalyst, chiefly solid paraffins of high melting point are produced at over 100 atm. pressure. It is now known that a catalyst life of 2 yr. or more can be expected at an operating pressure around 100 atm. and that increased pressure gives an increase in both yield and molecular weight of the paraffins produced. The reaction has been operated at 1,000 atm. with complete success. The catalyst is very sensitive to S; the concentration of S must be as low as 0.01 gm. per 100 $m.^3$ to prevent rapid poisoning. At 475°–500° and 30 atm. pressure with a catalyst of Cr oxide or Mo oxide, a gas 1 CO : 1 H_2 yields aromatic compounds. The factor of conversion is poor, and much CH_4 is formed; each $m.^3$ of synthesis gas yields up to 10 gm. of liquid containing about 50% aromatics and 50% naphthenes. The aromatics are chiefly xylene and toluene. At the high temperatures, C deposition is troublesome; an improvement can be secured by adding 5–10% of K_2CO_3 to the catalyst, but this slows the reaction rate. By means of methylation, with a catalyst of methyl chloride, Al chloride and Al metal, any lower paraffin may be converted into a more highly branched paraffin containing 1 more C atom. Thus far, success has been achieved only with the conversion of iso-C_4H_{10} to neopentane. This reaction proceeds to completion and n-C_4H_{10} isomerizes catalytically into iso-C_4H_{10} during the reaction, thus again giving neopentane; but iso-C_5H_{12} and the other butanes all yield neopentane again, being evidently decomposed into iso-C_4H_{10}.

701a. DeWitt, C. C., and Hein, L. B., Partial Oxidation of Light Hydrocarbon Gases at Atmospheric Pressure. Michigan State Coll. Agr., Eng. Expt. Sta., Bull., vol. 106, 1946–1947, 40 pp.; Chem. Abs., vol. 42, 1948, p. 857.

Partial oxidation of CH_4, C_2H_6, C_3H_8, and natural gas to HCHO and HCOOH was investigated over the range 350°–650° at 739 mm. pressure. Catalysts employed were electrolytic Cu, SiO_2 gel, CuO–SiO_2, V oxides on SiO_2, Mo oxides on SiO_2, and bronze tubing. The yield from the oxidation of natural gas in the presence of a Mo oxide catalyst at 650° was of the order of 3%, calculated as the % of O_2 input resulting in useful product. Data on the effects of flow rates of the various reactants in the presence of different catalysts are given. The most active catalysts were found to be Mo oxide–SiO_2 and V oxide–SiO_2 in that order.

DeWitt, T. W. *See* abs. 377, 669, 2009, 2718.

Dewling, W. L. E. *See* abs. 2831.

d'Hont, M. *See* abs. 2460.

Didenko, P. D. *See* abs. 2.

Diebold, R. *See* abs. 3436, 3437.

Dieckmann, T. *See* abs. 1420.

Dienst, W. *See* abs. 1036.

702. Diepschlag, E. [Reduction of Iron Ore by Employing Higher Pressures.] Arch. Eisenhüttenw., vol. 10, 1936, pp. 179–181; Chem. Abs., vol. 31, 1937, p. 635.

Complete separation of the O from the Fe in the ore is possible only at temperatures over 1,000°. Lower temperatures can, however, be used with fully the same efficiency and economy if the reduction is carried out at higher pressures, which increases velocity of reduction as the reduction gases penetrate faster into the interior. The reduction is greatest for pressures up to 3 atm. and more efficient in an atmosphere of CO than of H_2. The following reactions take place: $3Fe_2O_3+H_2=2Fe_3O_4+H_2O$; $Fe_2O_3+H_2=2FeO+H_2O$; $Fe_2O_3+3H_2=2Fe+3H_2O$; $3Fe_2O_3+CO=2Fe_3O_4+CO_2$; $Fe_2O_3+CO=2FeO+CO_2$; $Fe_2O_3+3CO=2Fe+3CO_2$.

Dieter, W. E. *See* abs. 1448.

Diethelm, A. *See* abs. 1616.

Dilthey, P. *See* abs. 978, 979, 980, 981, 1043.

Dimock, W. R. *See* abs. 3747.

Dinerstein, R. A. *See* abs. 3767, 3768.

Dingmann, T. *See* abs. 3052, 3053, 3055, 3057, 3059, 3061.

Dittrich, E. *See* abs. 3456.

703. Dobychin, D. P., Roginskii, S. Z. and Tsellinskaya, T. F. [Increasing the Activity of Nickel Formate Catalysts.] Jour. Phys. Chem. (U. S. S. R.), vol. 13, 1939, pp 1367–1388; Chem. Abs., vol. 35, 1941, p. 373.

Activities of $Ni(CHO_2)_2$ catalysts obtained at various temperatures, 150°–300° in vacuo and in a stream of H_2, were determined by means of the I numbers of the oils obtained by hydrogenation in their presence. Catalysts obtained in a stream of H_2 were as much as 5 times as active as those obtained in vacuo. Up to 245°, a higher temperature yields a more active catalyst, 2–3-fold at 220°–245°; further heating again yields less active catalysts because of rapid aging. The temperature should be brought up to the optimum as rapidly as possible. Similar results should be found for other catalysts produced by endothermic reactions. Catalysts prepared from $Ni(HCO_2)_2$ suspended in oil are more active than those prepared from the dry salt; the oil produces a more disperse catalyst by hindering recrystallization and sintering. Experimental data under various conditions and the activity of catalysts obtained are shown in 9 tables and 17 figures. In the initial stages the rate is given by the equation for a topochemical reaction, $\sqrt[3]{p}=\alpha+\beta t$. After a surface layer of Ni covers the formate crystal, the rate of decomposition is given by $v=k(a-x)^{2/3}$. For decomposition in oil, the initial rate is given by $v=At^3-Bt^4$.

704. Dodge, B. F. Note on the Methanol Equilibrium. Ind. Eng. Chem., vol. 22, 1930, pp. 89–90; Chem. Abs., vol. 24, 1930, p. 1018

Discrepancies between calculated values for K_p and those experimentally determined for the MeOH synthesis may be accounted for by lack of extreme accuracy for heats of reaction, since the quantity sought is the result of differences of larger quantities. Thus, if the value for heat of combustion for MeOH were in error 0.1%, K_p for the reaction at 298.1°, K would be in error 33%.

———. *See* abs. 1511, 2303, 2456, 2457, 2458, 3583.

705. Doehlemann, E. [Rates of Decarburization and of Carburization of Iron, Nickel, and Cobalt in Carbon Monoxide–Carbon Dioxide Mixtures.] Ztsch. Elektrochem., vol. 42, 1936, pp. 561–569; Chem. Abs., vol. 30, 1936, p. 8120.

Velocities of carburization and decarburization of Fe, Co, and Ni foils in stagnant CO–CO_2 mixtures at 920°–970° were determined by following the change in electrical resistance with a Kelvin bridge. Under the experimental conditions employed, the reaction at the metallic surface is the rate-determining factor. Diffusion within the metal proceeds rapidly. Data from the experimental curves show that the decarburization velocity is independent of the C content of the metal and increases linearly with the total pressure for a constant ratio of the partial pressures P_{CO_2}/P_{CO}. Carburization or decarburization velocities can be expressed as $-dc/dt=[K_1P_{CO_2}+K_2(P_{CO_2}/P_{CO})]\ [1-(c_t/c)]$, where K_1 and K_2 are graphically determined velocity constants while c_t and c are the C contents in weight % in the metal at equilibrium and at time t. From the 1st bracketed expression it can be seen that the reaction CO_2 (gas)⇄CO+O (adsorbed) determines the velocity of the process, while the reaction O (adsorbed)+C⇄CO is essentially in equilibrium. Values of 0.078, 0.155, and 0.308 for the CO_2: CO ratio were employed. These corresponded to solubilities of 0.42, 0.20, and 0.087 gm. C: 100 gm. Fe. Carbides do not precipitate at these temperatures until a solubility of C in Fe of 1 gm.: 100 gm. is obtained. As the solubilities of C in Co and Ni at these temperatures are smaller than for Fe, CO_2: CO ratios of 0.036, 0.082, and 0.108 were used for these metals. Plots of $dc:dt$ *vs.* reaction pressure for Co and Ni were similar to those for Fe, and the curves for all 3 metals can be similarly expressed. Different carburization rates may be found for 2 samples of Fe otherwise considered to be identical.

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706. ———. [Mechanism of the Water-Gas Reaction on an Iron Catalyst.] Ztschr. Elektrochem., vol. 44, 1938, pp. 178–183; Chem. Abs., vol. 32, 1938, p. 4060.

Velocity of the reaction $CO_2+H_2\rightarrow CO+H_2O$ on an Fe-foil catalyst at 910° is essentially proportional to the CO_2 pressure and increases with H_2 pressure somewhat more slowly than corresponds to a direct proportionality. The stationary C concentration of the Fe catalyst in a water-gas mixture, which is reacting in the direction $CO_2+H_2\rightarrow CO+H_2O$, is greater than corresponds to the equilibrium : C (dissolved in γ–Fe)+CO_2 (gas)⇄2 CO (gas). This qualitative result agrees with the working hypothesis that the catalytic water-gas reaction can be explained as a transfer of an O atom from CO_2 to H_2 through the formation of adsorbed O on Fe as an intermediate product; thus, (1) formation of O (adsorbed) as a relatively slow reaction: CO_2 (gas)⇄CO (gas)+$O_{(ads)}$: It is followed by (2) a rapid reaction (practically at equilibrium); $O_{(ads)}+H_{2(gas)}\rightleftharpoons H_2O_{(gas)}$: Then (3) a rapid reaction of C dissolved in Fe; $C_{(dissolved\ in\ \gamma\text{-}Fe)}+O_{(ads)}\rightleftharpoons CO_{(gas)}$. The data obtained did not confirm this mechanism quantitatively, probably because of simultaneous reactions.

Doherty, H. G. *See* abs. 3154.

707. Doherty, J. D. Synthetic Fuels Development. Oil Gas Jour., vol. 47, No. 28, 1948, pp. 207, 419; Min. Eng., vol. 1, No. 4, 1949, pp. 116–124: Am. Inst. Min. and Met. Eng., Tech. Pub. 2562 F.

Paper was presented at the annual Fuels Conference of the American Society of Mechanical Engineers and the American Institute of Mining and Metallurgical Engineers. Because "synthetic liquid fuels are not going to do us very much good in an emergency if we have to start from scratch," construction of commercial plants for the production of 1,000,000 bbl. per day should begin at once. The planned program calls for a total investment in plant and equipment of 8.7 billion dollars as compared with the 7.5 billion dollars that the petroleum industry will spend between 1947 and 1951 to maintain its present production rates. In general 2 processes would be used about equally: The Fischer-Tropsch gas-synthesis process and the Bergius coal-hydrogenation process. The cost of production per gallon of total products would be 12.4 or 12.6 cents depending on the process used. The production of 1,000,000 bbl. per day would consist of 86,000 bbl. liquefied propane and butane, 648,000 bbl. high-grade motor gasoline, and 266,000 bbl. Diesel and furnace oils. The coal requirement would be 575,000 tons per day, a 34% increase over the average 1947 production. Of this consumption, 213,000 tons would be bituminous coal from east of the Mississippi River and 362,000 tons would be coal and lignite from the West. Steel requirements are estimated at 6.3 million tons, the peak consumption occurring 5 or 6 years after starting the program. Employment would be given to about 160,000 men, including miners.

———. *See* abs. 644.

708. Doherty, T. B. Hydrocarbon Synthesis. Eng. Jour., vol. 31, 1948, pp. 425–429; Chem. Abs., vol. 42, 1948, p. 9116.

Possibilities of producing synthetic liquid fuels from coal or natural gas are discussed. German methods and plants are described as well as the American methods of preparing synthesis gas and the proposed method of processing coal for its production. The long-range United States development of synthetic fuels is most likely to be from coal. While in Canada the gas process is economically more attractive, it is unlikely that synthesis will be started in Canada in the near future. Reasons are given for this conclusion.

709. Dohse, H. [Heterogeneous Decomposition Reactions. III. Decomposition of Methanol on Zinc Oxide.] Ztschr. physik. Chem., vol. 8, Abt. B, 1930, pp. 159–180; Chem. Abs., vol. 24, 1930, p. 4452.

CH_3OH dissociates in 2 steps; 1st. into HCHO and then to $CO+H_2$. This can be seen with certainty only when studied from monomolecule films, and both steps are then of 1st. order. The reaction constants grow somewhat smaller as the reaction proceeds as a result of lessening activity of the reaction centers. The heat of activation for the 1st. is 22,500 cal. and for the 2d. 35,000 cal., the latter being in good accord with the direct determination for HCHO.

710. ———. [Catalytic Gas Reactions.] Chem. Fabrik, vol. 11, 1938, pp. 133–139; Chem. Abs., vol. 32, 1938, p. 4060.

Gaseous, liquid, and solid catalysts are discussed briefly, with examples to illustrate the reacting materials, temperature, pressure, catalyst, and products. The mechanism of catalysis, catalyst formation, and loss of activity by contraction from overheating and from poisoning are explained. A flow diagram, 5 views, and a model of a 75,000-ton plant for the manufacture of motor fuel from coal by the Fischer and Tropsch method are shown, and also cuts of apparatus for H_2SO_4 manufacture, including the Lurgi apparatus for direct conversion of H_2S into H_2SO_4.

Dokkum, T. *See* abs. 3043.

711. Dolch, M., and Kollwitz, J. [Reaction of Water Vapor Upon Glowing Coke. Contribution to the Oxidation of Coal.] Braunkohle, vol. 31, 1932, pp. 607–610, 628–632, 645–649; Chem. Abs., vol. 26, 1932, p. 5735.

In studying effects of rate of steam flow upon composition of gas formed, the reaction $C+H_2O=CO+H_2$ with bituminous cokes is found to be more rapid, and the reaction $C+2H_2O=CO_2+2H_2$ is more rapid with brown-coal cokes. With cokes of intermediate coals, this distinction is not noted. Thus, not only temperature and time, but the constitution of coal determine gas consumption. Apparatus for coke gasification with measured amounts of steam is described.

712. Dolch, P. [Action of Steam on Coal. Study of Superimposed Equilibria.] Ztschr. Elektrochem., vol. 38, 1932, pp. 596–601; British Chem. Abs., 1933, B, p. 5; Chem. Abs., vol. 26, 1932, p. 5193.

Action of steam on coal leads to the formation of CO and H_2. The formation of CO_2 is a secondary reaction ($CO+H_2O=CO_2+H_2$), the extent of which depends on the active coke surface. There is no evidence for the reaction $C+2H_2O=CO_2+2H_2$. Experiments with CO_2 and H_2, which were passed over coke, confirm this.

713. ———. [Water-Gas Generation From Coke and Coal.] Gas- u. Wasserfach, vol. 75, 1932, pp. 807–811; Chem. Abs., vol. 27, 1933. p. 399.

Calculations from the experiments of Bunte and Dolch show that the reaction of water vapor on C and the formation of CO_2 is determined by the water-gas equilibrium rather than by the water-gas reaction. The degree of attainment of the water-gas equilibrium depends on the reactivity of the coke on which the reaction takes place. No evidence is found for the direct action of water vapor on C according to the reaction $C + 2H_2O = CO_2 + 2H_2$. Experiments with mixtures of CO_2 and H_2 over wood charcoal at temperatures of 600°–1,000° indicated that CO_2 and H_2 first react to form CO and H_2O at about 600°, while CO_2 first begins to react with C at about 750°; with coke the corresponding temperatures are 800° and 980°. The significance of coke reactivity for technical water-gas manufacture is outlined, showing that a very reactive coke is desirable for the run, but that it leads to an excessive CO content during the blow period. Special adjustments of blow and run periods are required with the very reactive brown-coal coke. High reactivity is desirable, however, for the newer continuous water-gas processes using recuperators. The use of cokes from young coals should permit the manufacture of gas high in H_2 and CO_2, from which the CO_2 can readily be washed out to give a gas with high H_2 content for synthesis purposes.

714. ———. [Water-Gas Generation From Coal and Coke.] Gas- u. Wasserfach, vol. 75, 1932, p. 974; Chem. Abs., vol. 27, 1933, p. 827.

Reply to abs. 1412 and 2436. The attainment of the water-gas equilibrium depends more on the reactivity of the carbonization product than on the ash content. In general the degree attainment of this equilibrium parallels the reactivity of various cokes with respect to water vapor as given by Bunte (abs. 407). Experiments at 800° with a beechwood charcoal containing 2.3% ash indicated substantial attainment of the water-gas equilibrium as did experiments with a coke containing 5.3% ash. Both charcoal and coke were prepared by carbonizing the wood or coal at 1,000°

715. ———. [Influence of the Reactivity of Cokes on the Behavior of Carbon Dioxide-Hydrogen Mixtures at 600°–1,200°.] Brennstoff-Chem., vol. 14, 1933, pp. 261–263; British Chem. Abs., 1933, B, p. 772; Chem. Abs., vol. 27, 1933, p. 5173.

Both bituminous coke and wood charcoal accelerate the reaction $CO_2+H_2\rightarrow CO+H_2O$. Equilibrium was not reached during passage of a 3 : 7 mixture over the coke even at 970°; above this temperature interaction of the coke with the gases began, but even at 1,100° there were still appreciable quantities of steam in the efflux gases; below 820° with 34 : 66 mixtures with coke or charcoal, respectively, solid C does not enter into the reaction. Equilibrium in the gaseous reaction was reached over the charcoal at 750°; above 820° the gases reacted with it, and at about 1,000° only CO and H_2 were produced.

716. ———. [Chemical Principles of Synthesis-Gas Production. I. Water-Gas Equilibrium.] Feuerungstech., vol. 27, 1939, pp. 1–5; British Chem. Abs., 1939, B, p. 684; Chem. Abs., vol. 33, 1939, p. 3997.

In a discussion of the water-gas equilibrium as the chemical basis of synthesis-gas production, $H_2 : CO = 2$, the author compares the direct method of production in which all the water gas is passed through the catalyst vessel and conversion with steam continues until $H_2 : CO = 2$, and the indirect method in which some of the water gas is converted with steam into a gas with a low proportion of CO (2–4%) and this gas is mixed with the remaining water gas to obtain the desired ratio $H_2 : CO = 2$. The quantity of synthesis gas produced by the 2 methods is the same, but the steam consumption differs considerably.

717. ———. [Chemical Principles of Synthesis-Gas Production. II. Composition of Synthesis Gases. III. Yield of Synthesis Gas.] Feuerungstech., vol. 27, 1939, pp. 41–51; British Chem. Abs., 1939, B, p. 684; Chem. Abs., vol. 33, 1939, p. 3997.

Discusses the composition of synthesis gas and its dependence on the H_2 available. Explains ternary diagrams and derives equations to determine the effect of the H_2 available on the yield of synthesis gas. Discusses effects of methods of procedure and the CH_4 content of the gas.

718. ———. [Production of Synthesis Gas by Oxygen-Steam Gasification.] Feuerungstech., vol. 27, 1939, pp. 103–108; British Chem. Abs., 1939, B, p. 684; Chem. Abs., vol. 33, 1939, p. 5157.

After a general discussion of the chemical theory and the consumption of heat and O_2, the author describes briefly technical processes for producing synthesis gas by gasification with O_2-steam mixtures; that is, the Winkler producer, O_2-steam gasification in vertical ovens, the Lurgi process under pressure, and also the effect of the formation of CH_4 on the yield and composition of the gas. It is claimed that gasification in vertical ovens at atmospheric pressure with O_2-steam mixture produces a synthesis gas containing little CH_4 with the smallest O_2 consumption.

719. ———. [Synthesis Gas From Brown Coal. Fundamentals.] Brennstoff-Chem., vol. 20, 1939, pp. 101–111; Chem. Abs., vol. 33, 1939, p. 9592.

Brown coal as a raw material for producing synthesis gas is examined in detail in low-temperature assays, composition, and yield of products from 3 mid-German and 1 Bohemian brown coals of varying tar contents. Data obtained were analyzed in material balances and presented graphically. From the calculated proportions of the various constituents in the products, behavior of these coals in the Bubiag-Didier process with (1) simultaneous tar degasification, (2) tar removal and return of detarred gases, (3) complete gasification with outside heat, and (4) gasification with tar recovery and outside heating; in the Wälz gas process of Pintsch-Hillebrand and Koppers; and in the O_2-steam gasification of the Winkler suspension and pit processes, has been predicted with detailed yield data. Comparison indicates that the last-named process, in which heat-requirements of the gasification are met by separate gasification of part of the fuel, is far superior in yield of synthesis gas, particularly $CO+H_2$.

720. ———. [Development of the Koppers Continuous Vertical Retort in the Past 25 Years.] Gas- u. Wasserfach, vol. 86, 1943, pp. 27–33; British Chem. Abs., 1945, I, B, p. 118.

Kopper's installation for producing synthesis gas for noncoking Japanese long-flame coal of low ash-melting point is described.

720a. ———. [Reactions in Water-Gas and Synthesis-Gas Generation and Their Presentation in the Terbeck Diagram.] Gas- u. Wasserfach, vol. 93, 1952, pp. 234–238; Chem. Abs., vol. 46, 1952, p. 7,737.

Terbeck diagram has been shown to be useful for operational control and in the interpretation of gas analyses for synthesis gas plants. This diagram is also of value in planning, developing and placing such plants in operation. The graphic method presented in this article is simple and gives close agreement with practice.

721. Dolgov, B. [Synthesis of Liquid Fuel From Gases Obtained in Underground Gasification of Coal.] Podzemnaya Gazifikatsiya Uglei, No. 5, 1935, pp. 10–18; Chem. Abs., vol. 30, 1936, p. 1541.

Review. 19 refs.

722. Dolgov, B. N. [Methanol Synthesis. I.] Jour. Chem. Ind. (U. S. S. R.), vol. 8, 1931, pp. 457–472; Chem. Abs., vol. 25, 1931, p. 5139.

Review of well-known methods for industrial production of synthetic MeOH.

723. ———. [Methanol Synthesis. II.] Khim. Tverdogo Topliva, vol. 3, 1932, pp. 185–204; Chem. Abs., vol. 28, 1934, p. 5211.

Synthesis was carried out in a steel bomb lined with Cu and having a Cu insert to hold the catalyst. The process was effected at a cold pressure of 100–150 atm. and 350°–400°. Pure Kahlbaum CO and H_2 were used containing H_2, 97.2; CH_4, 0.4; unsaturated compounds, 0.2; N_2, 2.6; and O_2, 0.3%. Cu catalysts are not recommended, but good results were obtained with Zn chromates. Among the best tricomponent catalysts were $Cu_{49}Zn_{43}Cr_8$ and $Cu_{50}Zn_{40}Bi_{10}$, the yield of MeOH amounting to 86–87% and 75%, respectively, at temperatures of 360° and 400°. The product contained MeOH 89–92%, unsaturated compounds 2–4%, aldehydes and ketones 0.05–0.2%, and H_2O and other admixtures 9–4%. Various reactions are described. The difficulties in determining the amount of H_2O accompanying MeOH were overcome by the construction of a special apparatus, the product being treated with CaO.

724. Dolgov, B. N., and Karpov, A. Z. [Methanol Synthesis. III. Synthesis From Commercial Gas and a Long-Life Catalyst.] Khim. Tverdogo Topliva, vol. 3, 1932, pp. 282–288; Chem. Abs., vol. 28, 1934, p. 5212.

Synthesis was carried out in the presence of $4ZnO.Cr_2O_3$ catalyst was prepared from 324.0 parts ZnO and 304.0 parts Cr_2O_3 by shaking in 5 l. of H_2O for 24 hr. The mass then was filtered through a Büchner funnel and pressed into long strips. The gas was a technical water gas containing varying amounts of H_2 and CO. Therefore H_2 was added to the required ratio. The process was carried out at a constant pressure, the best pressure being 250 atm., and 370°. The product was contaminated with Fe carbonyl, which precipitated out through the influence of air. The degree of conversion with each cycle amounted to about 9%, with a total yield of 63%.

725. Dolgov, B. N., and Bocharova, E. M. [Methanol Synthesis. IV. Catalytic Oxidation of the Synthetic Methanol to Formaldehyde]. Khim. Tverdogo Topliva, vol. 3, 1932, pp. 406–418; Chem. Zentralb., 1934, I, p. 2652; Chem. Abs., vol. 28, 1934, p. 5805.

According to the experiments described in detail, passage of the gas mixture over porous surfaces (glass, porcelain, C) yields minute amounts of HCHO. The metallic catalysts, except Ag and Cu, are of little use. The yields are slightly higher when the catalysts are compressed in the reaction tube. Metal oxides cannot be used, while catalysts prepared from Cu disks, which are placed close together, give a HCHO yield up to 42%. A catalyst composed of CuO alone or together with an activator gives CH_2O yields of 21–42%. The best results were obtained with Th and U catalysts, which yielded up to 41–42% of CH_2O. The apparatus used is described, and the numerical data are tabulated.

726. Dolgov, B. N., and Karpinskii, M. N. [Methanol Synthesis. V. Influence of Activators on the Zinc-Chromite Catalyst.] Khim. Tverdogo Topliva, vol. 3, 1932, pp. 559–568; Chem. Zentralb., 1934, I, p. 2652; Chem. Abs., vol. 28, 1934, p. 5805.

Following promotors were used in conjunction with the $4ZnO.Cr_2O_3$ catalyst: W, V, Th, Ce, La, Ta, and Zr. The experiments were carried out with a decreasing pressure, each being carried out for 60 min. with 500 cc. of the catalyst. The highest MeOH yields were obtained with the promotors (1%) ThO_2, ZrO_2 and TaO_2. The results are tabulated and plotted.

727. ———. [Methanol Synthesis. VI. Synthesis From Carbonic Acid and Hydrogen.] Khim. Tverdogo Topliva, vol. 4, 1933, pp. 69–79; Chem. Zentralb., 1934, I, p. 2652; Chem. Abs., vol. 28, 1934, p. 5805.

These experiments were carried out with a decreasing pressure and the activity of the catalysts was investigated at 226°–400°. In another synthesis carried out at constant pressure and with introduction of additional portions of gases during the process, a circulating Fischer retort of 4.5-l. capacity was used. The gas mixture was prepared by mixing CO_2 and H_2, compressing it, and keeping it in steel bottles. The reaction $CO_2+3H_2\rightarrow CH_3OH+H_2O$, as shown by the experiments, proceeds in 2 stages (1) $CO_2+H_2\rightarrow CO+H_2O$ and (2) $CO+2H_2\rightarrow CH_3OH$. The velocities of the reactions differ, depending upon the ratio of gases, temperature, catalyst, etc. 19 different catalysts and their mixtures were investigated, and it was found that the maximum lies at 300°–325°, that is, 75° lower than that for MeOH from CO and H_2. The following catalysts were used in various combinations: MgO, Fe_2O_3, ZnO, ThO_2, V_2O_5, Ce_2O_3, CuO, Ni_2O_3, CdO, MnO, and Cr_2O_3. The highest MeOH yields were obtained with ZnO+4.5% CdO+5% Fe_2O_3 and ZnO+2% Fe_2O_3+1% CuO, reaching 51.5% and 50%. However, when maintaining a constant pressure by the introduction of new portions of gas, working at 325°, 200–210 atm., and using the catalyst ZnO+5% CdO, the yield of CH_3OH could be raised to 63% by weight. Changes in the velocity of the flow of the gas mixture caused lower yields of MeOH because of the slowing down of the conversion of CO_2 to CO. The crude MeOH contained C_nH_{2n} traces, C_nH_{2n+2} none, HCHO none, AcH traces, AcOEt none, AcOH about 0.05–0.06%, and $Fe(CO)_5$ none. A pure 98% MeOH is obtained by distillation and rectification. The gas used in the synthesis consisted of 1 vol. CO_2/3–3.5 vol. H_2 with the admixture of 0.2–0.8% CO and 0.4–3.0% N_2.

728. Dolgov, B. N., Karpov, A. Z., and Veltistova, M. V. [Methanol Synthesis. VII.] Khim. Tverdogo Topliva, vol. 4, 1933, pp. 492–499; Chem. Abs., vol. 28, 1934, p. 6279.

Catalyst that was used previously (*see* abs. 724) and that still retained its activity was analyzed after 186 experiments. It contained ZnO, 78.1, Cr_2O_3, 18.3; Fe_2O_3, 0.3; and S, 2.0%. The missing 1.1% includes admixtures such as $ZnCO_3$ and $ZnSO_4$. The influence of the volume velocity of the mixture of gases on the MeOH yield was investigated; at 350 l./hr. the volume velocity is 35,600, the duration of contact 10.4 sec., and the yield of MeOH 750 gm./hr. The frequency of the discharge of the MeOH from the apparatus affects the yields considerably; on discharging every 5 min. during 1 hr., 457 cm.^{3} of MeOH is obtained; in discharging every 30 min., the yield is only 373 cc. In the experiments carried out with water gas alone, without the addition of H_2, an appreciable decrease in the activity of the catalyst takes place. With the increase of the amount of the H_2, through conversion of the CO and consequent formation of H_2O, the activity of the catalyst increases, remaining, nevertheless, below that existing in the presence of enough H_2. Small amounts of AcOH, EtOAc, AcH, allyl alcohol, acetone, Fe carbonyl, S, and H_2O are formed, in addition to 96% MeOH.

729. Dolgov, B. N., Karpinskii, M. N., and Silina, N. P. [Methanol Synthesis. VIII.] Khim. Tverdogo Topliva, vol. 5, 1934, pp. 470–474; Chem. Abs., vol. 29, 1935, p. 7275.

ZnS as such, or with the addition of 5% of CdS, MoS_2, and CuS, decomposes MeOH 100% at 300°–375°. ZnS, with the addition of 1% of the above admixtures and Sb_2S_5 decomposes MeOH 100% at 300°–325°. ZnO decomposes MeOH completely at a temperature exceeding 400°. The composition of the gas obtained is near the stoichiometric ratio $CO : H_2=0.5$ only for ZnS, further additions considerably increase the H_2 ratio, particularly the 1% admixtures (1.5–2.5 times). An addition of 1% of activators increases the activity of the catalyst noticeably, but it lowers the amount of CO in the gas. The catalysts may be suitable for MeOH synthesis carried out under pressure.

730. Dolgov, B. N. [Synthesis of Hydrocarbons From Carbon Oxide and Hydrogen Under Atmospheric Pressure.] Khim. Tverdogo Topliva, vol. 8, 1937, pp. 901–922; Chem. Abs., vol. 32, 1938, p. 4308.

Review in which 22 catalysts used in the synthesis are tabulated and their merits discussed.

———. *See* abs. 277, 278, 279, 280, 281, 282, 1578, 3557.

Dolgov, B. N., and Bocharova, E. M. [Methanol Synthesis. IV. Catalytic Oxidation of the Synthetic Methanol to Formaldehyde.] *See abs.* 725.

Dolgov, B. N., and Karpinskii, M. N. [Methanol Synthesis. V. Influence of the Activators on the Zinc–Chromite Catalyst.] *See* abs. 726.

———. [Methanol Synthesis. VI. Synthesis From Carbonic Acid and Hydrogen.] *See* abs. 727.

Dolgov, B. N., and Karpov, A. Z. [Methanol Synthesis. III. Synthesis From Commercial Gas and a Long-Life Catalyst.] *See* abs. 724.

Dolgov, B. N., Karpinskii, M. H., and Silina, N. P. [Methanol Synthesis. VIII.] *See* abs. 729.

Dolgov, B. N., Karpov, A. Z., and Veltistova, M. V. [Methanol Synthesis. VIII.] *See* abs. 728.

731. Domenicali, C. A. Magnetic and Electric Properties of Natural and Synthetic Single Crystals of Magnetite. Phys. Rev., vol. 76, 1949, p. 460; vol. 78, 1950, pp. 458–467; Chem. Abs., vol. 44, 1950, p. 7104.

732. Dominik, W. [Catalysts for the Reaction $CO+H_2O\rightleftharpoons CO_2+H_2$.] Przemysl Chem., vol. 11, 1927, pp. 557–562; Chem. Abs., vol. 23, 1929, p. 1997.

Process of preparing the catalyst was based on the equation: $3FeCO_3+HNO_3+4H_2O=3Fe(OH)_3+NO+3CO_2$. Its activity was still great at a temperature as low as 390° working with a gas composed of CO_2, 7.5, CO, 17, and H_2, 55%. The hypothesis was substantiated that only metal that possesses the least alkaline properties, and the sulfide of which is readily hydrolyzed by water vapor, can be a permanent activator in presence of S gases. Thus, it was possible to reactivate the Fe catalyst with Cr or Al but not with Co or Mn.

733. ———. [Catalysts for the Reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$.] Przemysl Chem., vol. 12, 1928, pp. 229–235; Chem. Abs., vol. 22, 1928, p. 4334.

From theoretical considerations the following equation for $CO + H_2O \rightleftharpoons CO_2 + H_2$ is derived:

$$\frac{x-x_2}{x-x_1}=\frac{x_0-x_2}{x_0-x_1}\cdot e^{-b(K-1)(x_1-x_2)1/V}.$$

This is like that for bimolecular reactions in homogenous systems. b is a constant that characterizes the useful surface of the catalyst at a given temperature, $K = [CO_2]\ [H_2] : [CO]\ [H_2O]$ = equilibrium constant at a given temperature, V = space velocity of the gas vapor mixture in cc. per hr. per gm. of catalyst, x = partial pressure of CO_2 in the reaction mixture, x_0 = partial pressure of CO_2 before the reaction, x_1 and x_2 the 2 roots of the equation

$$\frac{x(P_0H_2+x-x_0)}{\{P_0CO-(x-x_0)\}\{P_0H_2O-(x-x_0)\}}-K=0,$$ in which

P_0H_2, P_0CO and P_0H_2O represent the partial pressures of the respective components before the reaction, and only x_2, the root with the negative radical, represents the pressure of CO_2 at equilibrium. To test this experimentally the extent of the reaction was measured after the gaseous mixture had passed over 1 and over 2 equal portions of the catalyst under the same conditions. A whole series of determinations shows that the catalysis of water gas does proceed according to the derived equation, but that possibility of small differences of temperature lowers the accuracy of the determinations.

734. ———. [Processes for the Synthetic Production of Liquid Fuels.] Przeglad. Chem., vol. 2, 1938, pp. 14–17; Chem. Zentralb., 1939, I, p. 1698.

Review of processes for the production of fuels from coal, with comparative costs for the construction of plants in Poland.

Donath, E. E. *See* abs. 644, 3311.
Donn, L. *See* abs. 3392.
Dorcas, M. J. *See* abs. 1488.
Doring, W. *See* abs. 3570.

735. Dorschner, O. [Gas Pipeline Transmission of Methane Derived From Pressure Gasification and Synthesis.] Erdöl u. Kohle, vol. 2, 1949, pp. 59–65; Chem. Abs., vol. 43, 1949, p. 4832.

For obtaining a gas of high calorific value from the residual Fischer-Tropsch synthesis, a process has been developed that combines pressure gasification of coal with Fischer-Tropsch synthesis. Pressure gasification may be carried out with lignite or coal (moisture and ash content up to 35%, particle size 2–40 mm.) and an O_2-steam mixture at 10–30 atm. The exothermic CH_4 reaction reduces the O_2 consumption to ½ of that used in similar processes. The percentage compositions of the raw gas, synthesis gas (after removal of CO_2), and CH_4 gas (residual gas from Fischer-Tropsch synthesis) follow, respectively: CO_2, 28.6, 1.0, 3.9; C_nH_m, 0.9, 1.2, 1.8, CO, 18.7, 25.5, 2.7; H_2, 38.1, 53.3, 3.2; CH_4, 12.4, 17.2, 82.1; N_2, 1.3, 1.6, 6.3; heats of combustion in kcal. per m.^{3} were 3,150, 4,350, 8,450. There is no reduction in yield of liquid products nor in catalyst activity. The heat balance for ordinary synthesis gas: 3,066 kcal. = 100%; liquid hydrocarbons, paraffin 1,385 kcal. = 45%; residual gas 1,062 kcal. =34.7%; steam 414 kcal. = 13.6%; loss 205 kcal. = 6.7%. Heat balance for pressure gasification 4,135 kcal. = 100%; liquid products 1,240 kcal. = 30%; CH_4 gas 2,290 kcal. = 55.4%; steam 400 kcal. = 9.7%; loss 202 kcal. = 4.9%. The gas also may be utilized as fuel for motor vehicles, locomotives (gas turbines), or raw material for C_2H_2 manufacture. Diagram of process.

736. Dotterweich, F. H. Report of Subcommittee. I. On New Developments. Proc. Am. Gas Assoc., vol. 26, 1944, pp. 316–318.

Perfection of the steam conversion process for transformation of natural gas to blue gas or H_2 as end products has been of importance. The former is available for MeOH and HCHO production or as the first steps in the Fischer-Tropsch process. To date, research on this subject suggests the production of 1 bbl. of hydrocarbon liquid/10,000 cu. ft. of natural gas, including fuel for the process.

737. ———. Intrinsic Value of Natural Gas, a National Asset. Am. Gas Jour., vol. 165, No. 6, 1946, pp. 11–14, 58.

The role of natural gas in the national economy is presented, with brief mention of its utilization in producing liquid fuel by way of the Fischer-Tropsch and the Hydrocol processes.

———. *See* abs. 2661, 2662.

738. Dotterweich, F. H., and Huff, W. J. Colloidal Properties of Iron Oxide in Hydrogen Sulfide Removal. Proc. Am. Gas Assoc., vol. 20, 1938, pp. 699–717; Gas Age, vol. 82, No. 9, 1938, pp. 43–44, 54, 56–58; Chem. Abs., vol. 33, 1939, p. 1473.

Adsorption capacity, activity, and colloidal content of a number of Fe oxides used for removing H_2S from gas were measured. These oxides were divided into 2 groups, (1) those containing more than 11% Al_2O_3 and (2) those containing less than that amount. Oxides of group (1) showed increasing capacity and activity for H_2S absorption with decreasing particle size; those of group (2) showed greater activity but diminishing capacity with decreasing particle size. Also oxides of the latter group are affected markedly in their activity by changes in alkali content. Heating the oxides to 550° caused the particle size of all oxides to increase; this resulted in correspondingly lower activity.

739. D'Ouville, E. L., and Howe, K. E. Use of Thermal Conductivity Cells for Gas Analysis in Studying the Fischer-Tropsch Synthesis of Hydrocarbons. Petrol. Refiner, vol. 26, No. 6, 1947, pp. 526–531.

Method is described with the help of 11 figs. for analysis of both synthesis gas and product gas from a bench-scale Co-catalyst Fischer-Tropsch unit. A single thermal conductivity cell unit is used for binary mixtures and for other mixtures that can be so considered. For complex mixtures of as many as 5 components a multiple cell unit is described. A complete description of the cells, auxiliary equipment, and technique is given. The advantages and limitations of the method are discussed with special reference to Fischer-Tropsch gases.

740. Dowd, J. J., Elder, J. L., Capp, J. P., and Cohen, P. Experiment in Underground Gasification of Coal, Gorgas, Ala. Bureau of Mines Rept. of Investigations 4164, 1947, 62 pp.

Using various methods of operation, it was determined that gases could be generated specifically for use in generating power or for synthesis purposes. It is estimated that 236 tons of coal were burned completely and 164 tons coked during the combustion period. 5 types of blasting were used: Gas-air, O_2-air, O_2-air-steam, O_2-steam, and steam. Comparative heating values for each of these methods per cu. ft. of gas were, respectively: 47, 50, 110, 135, and 200 B. t. u. It was also determined that the first 2 methods produced gases suitable for power generation, while the last 3 yielded gases suitable for synthesis purposes.

741. Downs, C. R. Impact of Tonnage Oxygen on American Chemical Industry. Chem. Eng., vol. 55, No. 8, August, 1948, pp. 113–117, 121.

The paper was presented before the Chemical Market Research Association. Tonnage O_2 of 90–95% purity is being produced experimentally, and enormous plants for its production are being constructed. It will largely supplant 99.5% O_2, except for metal cutting and welding. Production of 99.5% O_2 now amounts to about 15.5 billion cu. ft./yr. 7 plants for production of 95% O_2 are now being built, the estimated production of which is 40 billion cu. ft./yr. The composition of 95% O_2 by vol. is approximately 95% O_2, 3.2% A, and 1.8% N_2. Plant and operating costs for a plant of 1,000 tons/day capacity should be $4,000,000 and $3.67/ton, respectively, whereas the cost of 99.5% O_2 is approximately $64–$120/ton, depending upon a monthly volume of 190–10 tons respectively. Several uses for tonnage O_2 are presented and discussed, such as synthetic fuels, chemicals, iron and steel production, roasting of ores, and city gas and chlorine production.

742. Downs, C. R., and Rushton, J. H. Tonnage Oxygen. Chem. Eng. Progress, vol. 1, 1947, pp. 12–20; Chem. Abs., vol. 41, 1947, p. 2213.

Potential examples for the use of tonnage oxygen are discussed at some length: Gasification of coal, synthesis gas production, synthetic liquid fuels, chemical products (Synthine process), H_2SO_4 and SO_2, and metallurgical uses. Costs are calculated as follows:

Estimated total plant and operating costs, October 1946, for producing 95% O_2

Plant capacity..........tons per day..	120	240	360	480	1,000
Plant capacity..........tons per hr..	5	10	15	20	42
95% O_2........million cu. ft. per day..	2.88	5.76	8.64	10.52	24.00
Approx. plant cost....million dollars..	.9	1.3	1.7	2.0	3.4
Total utility cost....dollars [1] per ton..	1.29	1.27	1.25	1.22	1.20
Operating labor per ton, $80 per day...	.68	.34	.23	.17	.08
Maintenance per ton, 2.5%..........	.54	.39	.34	.30	.25
Fixed charges per ton, 12.5%..........	2.70	1.95	1.70	1.50	1.22
Total operating cost per ton..........	5.21	3.95	3.52	3.19	2.75
Total operating cost per 1,000 cu. ft..........cents..	21.7	16.5	14.7	13.3	11.5
Kw.-hr. per 1,000 cu. ft. for compression..........	13.4	13.1	12.8	12.7	12.5
Kw.-hr. per 1,000 cu. ft. for auxiliaries.	2.2	2.2	2.2	2.2	2.2
Total kw.-hr. per 1,000 cu. ft..........	15.6	15.3	15.0	14.9	14.7

[1] Includes water, 1 cent per 1,000 gal.; incidental electric power, 0.4 cent per kw.-hr.; steam, 30 cents per 1,000 lb.

742a. Drain, J., and Michel, A. [Structure and Thermomagnetic Properties of the Cobalt Carbide Co_2C.] Bull. soc. chim., 1951, pp. 547–549.

By passing CO over Co at 210° Co_2C was formed. Its structure appears to result from the insertion of C atoms into an orthorhombic, almost compact hexagonal, network of Co atoms. This insertion gives rise to a series of solid solutions which may deviate from the composition Co_2C. The carbide Co_2C is only the upper limit. The paramagnetic carbide Co_2C is transformed under vacuum into a compact hexagonal phase which is a solid solution of C in α–Co, this phase being progressively decarburized by heating to give a pure hexagonal Co. The gases, H_2, N_2, CO, in accordance with their nature, react upon Co_2C and cause an evolution analogous to that which the hexagonal Ni carbide undergoes under the same conditions.

743. ———. [Thermomagnetic and Structural Study of the Cobalt Carbide Co_2C.] Bull. soc. chim., January–February 1951, p. 23.

Reduced Co, supported on ThO_2, was carburized with CO at 210° C. to form paramagnetic, orthorhombic Co_2C (abs. 1440) similar to Co_2N, with a=2.904Å, b=4.465Å, c=4.368Å. The crystalline parameters varied slightly with the mode of preparation, probably because of differences in composition. The carbide decomposed in vacuo at about 260° into a ferromagnetic hexagonal close-packed solid solution of C in α–Co, which was subsequently decarburized to hexagonal close-packed α–Co. Reaction set in at 298° in N_2, at 198° in H_2, and at 364° in CO.

744. Drawe, R. [High-Heating-Value Gas From the Oxygen Gas Producer.] Gas- u. Wasserfach, vol. 76, 1933, pp. 541–545; Chem. Abs., vol. 27, 1933, p. 5172.

At Tegel, brown coal was gasified at atmospheric pressure in an O_2 gas producer at the rate of 200 kg. per m.^{2} producer area. Higher rates were not possible because of limited O_2 supply. The O_2 was saturated at 89°–93°. No slagging was noted. With O_2 saturated at 90°, 1 m.^{3} O_2 gave 16,000–17,000 cal. in the form of gas having the following analysis: CO_2, 13.2%; O_2, 1.1%; illuminants, 2.3%; CO, 32.9%; H_2, 42.8%; CH_4, 1.1%; and N_2, 6.6%. 1 m.^{3} of O_2 was enough to gasify 4 kg. brown-coal briquets. Experiments with an O_2 gas producer at elevated pressures by the Lurgi Gesellschaft für Würmetechnik were limited by the O_2 supply to 900 kg. throughout per m.^{2} of producer area per hr. at an operating pressure of 20 atm. The back pressure with a 3-m. fuel bed was less than 50 mm. At the higher pressure tar oils and light oil were easily separated by cooling. The O_2 used had a purity of 72–73%, but calculations as to O_2 requirements were made on a basis of 90% O_2, indicating that requirements per 4,000 cal. in the form of gas were 0.202 m.^{3} at 1 atm., 0.110 m.^{3} at 10 atm., and 0.80 m.^{3} at 20 atm. operating pressure. The calculated heating value of the CO_2-free gases reached a maximum of 534 B. t. u. per cu. ft. at 20 atm., so that this gas should be satisfactory for city gas. An O_2 price equivalent to about $0.10 per 1,000 cu. ft. is assumed in estimating that this gas could compete with other sources of city gas.

745. ———. [Increasing the Form Value of Fuels.] Gas- u. Wasserfach, vol. 80, 1937, pp. 806–810; Chem. Abs., vol. 32, 1938, p. 1071.

Continuous gasification of brown coal with O_2 and superheated steam at 20 atm. is described. The town of Zittau has been supplied during the past year with gas of calorific value 4,280 kcal. per m.^{3} and d. 0.448. Modification of the process to produce liquid fuel by the Fischer-Tropsch synthesis could be made by operating at 8–10 atm.

746. ———. [Results of Pressure Gasification With Oxygen.] Arch. Wärmewirt., vol. 19, 1938, pp. 201–203; Chem. Abs., vol. 32, 1938, pp. 7700.

Plant of Zittau gasifying brown coal with mixed steam and O_2 at 20 atm. is briefly described with a heat balance. Curves are given to show that as the pressure increases the CH_4 and CO_2 in the products rise, while the H_2 and CO fall.

747. ———. [Evaluation of Fuels.] Glaser's Ann., vol. 73, No. 5, 1949, pp. 80–85; Gas- u. Wasserfach, vol. 90, 1949, pp. 212–217.

Discusses evaluation of solid, liquid, and gaseous fuels. Presents data on performance and heat consumption of various power gases and heat balance of the Fischer-Tropsch synthesis and of high caloric gas production.

Dressler, R. G. *See* abs. 155, 156, 1431, 1677a, 3549.

Drew, T. B. *See* abs. 607.

748. Drigo, A., and Pizzo, M. [Magnetization of Thin Ferromagnetic Films.] Nuovo cimento, vol. 5, 1948, pp. 196–206; Chem. Abs., vol. 42, 1948, p. 7587.

- [illegible] [illegible] 695-0678
- [illegible]
- [illegible] [illegible]

Preliminary paper. Theories of magnetism predict that the properties of thin films should differ from those of massive samples. Experiments with thin films of Fe, Co, and Ni show that the characteristics of the magnetization curve vary with film thickness. Barkhausen discontinuities disappear at a thickness of 1.2×10^{-5} cm. for Co, 0.8×10^{-5} for Ni, and 1.3×10^{-5} for Fe.

Drikas, G. *See* abs. 3140.

748. Dubrovskaya, A., and Kobozev, N. I. [Adsorption Properties of Promoted Iron Oxide in Relation to the Distribution of the Promoter in the Oxide Form of Ammonia Catalysts.] Acta Physicochim., U. R. S. S. (in German), vol. 4, 1936, pp. 841–858; Chem. Abs., vol. 30, 1936, p. 7987.

Adsorption isotherms of O_2 on pure Fe_2O_3 and on Fe_2O_3 that contained 10% Al_2O_3 were determined at −190° and +400°. X-ray photographs of Fe_2O_3 samples heated to various temperatures showed that the adsorbing power of Fe_2O_3 decreased as the crystals became larger. The kinetics of O_2 desorption from promoted and nonpromoted Fe_2O_3 studied at various temperatures, showed that the activation energy of desorption is independent of the presence of a promoter and averages 10,860 cal. Thus, even in the case of the promoted Fe_2O_3, the adsorption centers are the Fe_2O_3 mols. It was found that the addition of 10% Al_2O_3 to Fe_2O_3 lowers the specific adsorption of O_2. This proves that the dissolved Al_2O_3 is strongly adsorbed on the surface of the Fe_2O_3 crystals. From the data found, the equilibrium constant between the dissolved and adsorbed Al_2O_3 was calculated and an equation derived. Using this equation, it was shown that with relatively large Fe_2O_3 crystals, 1% Al_2O_3 shielded 50% of the surface of the Fe_2O_3.

750. Duchene, G., and Martin, R. M. [French Experimental Station for the Production of City Gas and Synthesis Gas From Fuveau Lignites.] Chaleur et ind., vol. 29, No. 274–275, May–June 1948, pp. 113–125, 149–156; Chem. Abs., vol. 42, 1948, p. 6514.

Description with diagrams and operating data of an experimental plant for the production of city gas and synthesis gas by the Syngaz process developed by G. Szigeth of Hungary. It appears to be a modification of the Woodall-Duckham system. The process is continuous and includes the phases of carbonization, water-gas production, and gas conversion in the same apparatus. The last step involves a reversal of the gas stream and cracking of the hydrocarbons and the CH_4 by contact with the incandescent coke. The results of two Syngaz runs reveal the production of synthesis gas with the correct CO : H_2 ratio of 1 : 2.

Dudash, A. P. *See* abs. 1987.

Dudley, J. F. *See* abs. 1677.

751. Duff, D. M. Coal Gasification Rather Than Hydrogenation Urged. Oil Gas Jour., vol. 46, No. 40, 1948, pp. 39, 129.

P. C. Keith, in a recent talk at a meeting of the Natural Gasoline Association of America, proposes, "coal gasification rather than expensive, inefficient coal hydrogenation," as a means of meeting the existing shortage of fuels. Use of 100,000,000 tons of coal per year in a noncatalytic, relatively simple, gas-from-coal process originally developed by the Germans and now under pilot-plant operation in Trenton, N. J., would replace the 350,000,000 bbl. of petroleum fuels, which the residual and distillate heating market is estimated to require annually by 1950. This shift, coupled with the 650,000 bbl. of liquid fuels per day considered as available from natural-gas conversion, might bridge the 2,000,000-bbl. daily gap, which has been mentioned by Government authorities. A program for the wholesale conversion of coal to liquid fuels, either by high-pressure hydrogenation or low-pressure Hydrocol process is unwise and ill-advised at present. Thermal efficiency of the coal-to-liquid-fuel processes is basically low (not over 45%) and there is a serious question if the tremendous quantities of coal required are readily available.

752. ———. Synthesis Fuels Competitive With Crude-Based Fuels. Oil Gas Jour., vol. 46, No. 37, 1948, p. 57.

According to E. V. Murphree, president of the Standard Oil Development Co. and principal speaker at the dedication of a new research building at Baton Rouge, motor fuel produced from natural gas is now generally competitive with that produced from petroleum. The hydrocarbon-synthesis process employing the fluid-catalyst technique is still undergoing improvement, and commercial plants are being considered. Comparative plant costs under present prices are about as follows: For a conventional refinery, \$2,000–\$2,500 per bbl. of product per day; for a natural-gas synthesis plant, \$4,000–\$4,500; and for a synthesis plant using coal, \$8,000. A pilot-plant demonstration of the 2-vessel system of shale retorting using the fluid technique will soon be inaugurated. Pilot plants devoted to synthesis study including a 10-bbl. per day unit from which data are being obtained through more than 60 recording instruments are under operation. A former hydrogenation unit is being converted to the production of higher molecular-weight alcohols, the process, therefore, being based on the reaction between synthesis gas and certain petroleum fractions with subsequent hydrogenation.

753. Dumanois, P. Utilization of Methanol as a Possible Automobile Fuel. Oil Gas Jour., vol. 25, No. 28, 1926, p. 142; Proc. Internat. Conf. Bituminous Coal, 1st Conf., 1926, pp. 161–164; Chem. Abs., vol. 21, 1927, p. 2179.

Objections to the use of MeOH as fuel are its low calorific value and the tendency to form aldehydes on incomplete combustion. At compression ratios above 6, the alcohol caused self-ignition. Detonation may be eliminated by the use of an antidetonant such as $PbEt_4$.

Dunning, R. G. *See* abs. 2035.

754. Dunstan, A. E. Fluid Fuels. Gas and Oil Power, vol. 22, No. 253, 1926, pp. 6–7.

Deals with Bergius process and synthol.

755. ———. Refining of Petroleum. III. Synthol and Synthetic Petroleum. Fuel, vol. 8, 1929, pp. 502–504. Chem. Abs., vol. 24, 1930, p. 2587.

Excerpt from the Cantor lecture. Briefly reviews work of Badische Anilin- und Soda-Fabrik, Patart, Fischer, and Tropsch on the synthesis of hydrocarbons from CO and H_2.

756. ———. Fluid Fuels Today and Tomorrow. Chem. and Ind., vol. 51, 1932, pp. 822–831, 846–855; Chem. Abs., vol. 27, 1933, p. 176.

Second jubilee memorial lecture. Discusses liquid fuels from various sources: Petroleum, natural gas, bottled gas, coal carbonization, and synthetic oils.

757. Dunstan, A. E., and Shatwell, H. G. Liquid Fuels Other Than Petroleum. Jour. Inst. Petrol. Technol., vol. 14, 1928, pp. 64–77; Chem. Abs., vol. 22, 1928, p. 1845.

Consideration of liquid fuels obtainable from low-temperature carbonization, coal hydrogenation, and gas reactions is shown. Results from low-temperature carbonization have been disappointing. Of the 16-gal. primary tar per ton of coal obtained, about ⅓, which is tar acids and bases, must be removed, unless the tar is to be used in boilers or Diesel engines. The remaining tar contains paraffins, wax, pitch, and unsaturated hydrocarbons. The latter resist detonation in internal-combustion engines and are thus especially useful in blending. In hydrogenation, the technical validity of the Bergius process is established, 1 ton

of coal producing 140 gal. of liquid product resembling low-temperature primary coal tars. Recovery of H_2 is important economically, and methods for doing this are mentioned. Gas reactions afford many possibilities and variations. Catalytic reduction of CO at high pressures yields oxygenated compounds. At atmospheric pressure and high temperature, CH_4 is the sole product. Synthetic MeOH can be obtained with almost theoretical yield by using ZnO at 400° and 150 atm. For this purpose other catalysts mentioned are metals and metallic oxides or their mixtures, salts, oxides of Cu, Ag, Zn, Pb, or Cd, chromates, vanadates, molybdates, and tungstates, but Fe, Ni, and Co must be rigorously excluded. For products other than MeOH, iron metals and alkalies are essential. Synthol, a mixture of higher alcohols, fatty acids, aldehydes, ketones and esters, but no hydrocarbons, is obtained by passing water gas over Fe borings impregnated with a strong base at 410° and 50 atm. Fischer and Tropsch have obtained gaseous liquid and solid homologs of CH_4 by low-temperature reduction of CO. Gives references to literature and to patents.

Dunville, T. C. *See* abs. 3549.

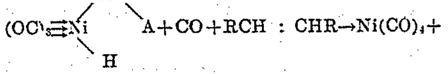
758. Dupas, M. R. [Lubricant Synthesis.] Bull. assoc. franç. techniciens petrole, No. 69, 1948, pp. 1–16; Jour. Inst. Petrol., vol. 34, 1948, p. 265 A; Chem. Abs., vol. 43, 1949, p. 1952.

After a brief review of the chief methods for lubricating-oil synthesis, describes (with flow sheet) the process used at the Standard-Kuhlmann plant at Estaque. Lubricating oil is produced by a Friedel-Crafts condensation of benzene with dichlorethane and a Fischer-Tropsch gas oil (180°–320°) chlorinated to a Cl content of 22–24%. Production is effected continuously in 3 steel vessels; in the 1st vessel (at 80°) benzene, dichlorethane, and Al powder are mixed. The chlorinated gas oil is added in the 2d stage (at 100°), and the reaction is concluded in the 3d vessel (at 120°). Flow through the plant takes 6 hr. The supernatant oil is separated from the $AlCl_3$ residue, neutralized with Na_2CO_3 solution, and the excess benzene is removed by distillation. Following a clay treatment to eliminate traces of $AlCl_3$ the product is vacuum distilled yielding 2 side streams (transformer and light engine oils), and a residual bright stock. Gas oil is removed overhead and recycled. A further quantity of secondary oil, together with benzene and gas oil, is recovered by hydrolysis of the $AlCl_3$ residue. The yields (as % on the hydrocarbon charge) are: primary oil, 45%; secondary oil, 10%; recycle, 27%; and loss, 18%. The viscous oils (35–330 cs. at 50°) obtained have high density (0.942–0.950) and good viscosity index.

DuPont, G. *See* abs. 1260.

759. DuPont, G., Piganiol, P., and Vialle, J. [The Oxo Reaction and Its Mechanism.] Bull. soc. chim., France, 1948, pp. 529–532; Chem. Abs., vol. 42, 1948, p. 7232.

Instead of the formation of the intermediate $\underbrace{\mathrm{RCH\cdot CHR\cdot CO}}$ (I) when CO reacts with olefins in the presence of metallic carbonyls, the authors propose the existence of a combination of Ni or Co carbonyl with a reactive compound, A.H (H_2, H_2O, ROH, R_2NH, etc.). This complex (II) reacts with the olefin in the presence of CO to regenerate the metal carbonyl and give III:



$$(\mathrm{OC})_3 \rightrightarrows \overset{\mathrm{C:O}}{\underset{\mathrm{H}}{\mathrm{Ni}}}\mathrm{A} + \mathrm{CO} + \mathrm{RCH : CHR} \rightarrow \mathrm{Ni(CO)_4} +$$

$\underset{\substack{| \\ \mathrm{AC:O}}}{\mathrm{RCHCH_2R}}$ (III). It is stated that number I has been isolated from these reactions and that they do not occur unless A.H is present. C_2H_2, CO and $Ni(CO)_4$ in the presence of a little HCl and alcohol at 50° give a 50% yield of polymers of $CH_2 : CHCO_2Et$ and $CH_2 : CHCO_2H$. 1-Hexene, alcohol, CO, and $Co(CO)_4$ at 180° and 300 kg. pressure for 7 hours give 70% of a mixture of $Me(CH_2)_5CO_2Et$ and $Me(CH_2)_3$ $CHMeCO_2Et$. Cyclohexene under similar conditions gives 37% $C_6H_{11}CO_2Et$. Replacing the alcohol with H_2O gives the acid. Me hendecenoate gives a mixture of diesters. Compounds with double bonds next to a tertiary C (carvomenthene and pinene) give little, if any, reaction.

760. Durand, J. F. [Double Decomposition of Metallic Acetylides and Salts in an Aqueous Medium.] Compt. rend., vol. 177, 1923, pp. 693–695; Chem. Abs., vol. 18, 1924, p. 657.

CaC_2, when added to aqueous solutions of salts, precipitates acetylides, which can be purified by washing with dilute HOAc. Thus, with $CuCl_2$, CuC_2; with $NiCl_2$, NiC_2; with $MnCl_2$, MnC_2; $FeCl_2$, FeC_2.

761. Dutta Roy, R. K. Synthetic Gasoline in India. Jour. Indian Chem. Soc., Ind. News Ed., vol. 12, No. 2, 1949, pp. 28–48; Chem. Abs., vol. 44, 1950, p. 2729.

Discusses available processes for the production of synthetic liquid fuels and their status in various countries. Gasoline production in India can meet only 10% of the demand. The Bergius and Fischer-Tropsch processes are reviewed concerning their requirements for raw material and synthesis-gas manufacture. Describes plant layout.

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761a. Eastman, D. Preliminary Report on Coal Gasification. Am. Inst. Min. and Met. Eng., 173d Meeting, February 1952.

According to the Texas Co., any type of coal can now be processed into synthesis gas under high pressure. A slurry of finely ground, raw coal containing 40–60% coal and 60–40% H_2O is pumped through a heater, where the coal suspension is raised to several hundred pounds pressure and temperatures exceeding 1,000° F., into the reaction chamber where it meets a stream of pure O_2. The ash which has become molten is drawn off at the bottom of the reaction chamber into a reservoir of cold H_2O where it disintegrates and is removed as a finely divided solid suspended in H_2O. The product gas passes through a waste-heat boiler. The reactor, a pressure shell fitted with an internal coil, has H_2O circulating through it. The generator is normally operated at a temperature above the fusion point of the ash. If the fusion temperature is higher than the desired reaction temperature, a fluxing agent may be added to the coal-H_2O feed to help melt the ash. Gasification has been as high as 95%. O_2 consumption rates are expected to be 15,000–20,000 ft.³ per ton of dry coal with 80–90% of the heating value of the coal appearing as H_2 and CO in the synthesis gas.

762. Eastman, E. D. Equilibria in the Systems: Fe–C–O and Fe–H–O, and the Free Energies of the Oxides of Iron. Jour. Am. Chem. Soc., vol. 44, 1922, pp. 975–998; Chem. Abs., vol. 16, 1922, p. 1901.

Summary of the widely scattered and often discordant data relating to the oxides of Fe and to the equilibria in which they are involved, with an attempt to appraise and interpret the results. For each of the reactions: $3FeO + CO_2 \rightleftharpoons Fe_3O_4 + CO$, $Fe + CO_2 \rightleftharpoons FeO + CO$, and $3Fe + 4CO_2 \rightleftharpoons Fe_3O_4 + 4CO$ the equilibrium constant (CO_2) : (CO) has been plotted for different temperatures. The lines for the 3 reactions meet in the invariant point, where there are 3 solid phases and a gas phase (theoretically the C occurs only in the gas phase) at about 560° and (CO_2) : (CO)=1. Similarly for the reactions: $FeO+H_2 \rightleftharpoons Fe+H_2O$, $Fe_3O_4+H_2 \rightleftharpoons 3FeO+H_2O$, and $Fe_3O_4+4H_2 \rightleftharpoons Fe+4H_2O$ the lines meet at about 560° and where (H_2) : (H_2O)=4. The free energies of the oxides of Fe have been calculated by means of the relation, $\Delta F= -RT\ln K$.

763. Eastman, E. D., and Evans, R. M. Equilibria Involving the Oxides of Iron. Jour. Am. Chem. Soc., vol. 46, 1924, pp. 888–903; Chem. Abs., vol. 18, 1924, p. 1418.

Compositions of the gas phase in equilibrium with solid phases varying in average composition between pure Fe and Fe_3O_4 have been determined at 772° in the system Fe : H_2 : O_2. The results indicate the existence at this temperature of solid solutions in the composition ranges 0–5% O_2, 20–24% O_2, and above about 27% O_2. Equilibrium constants in the divariant equilibrium in this system represented by the equations, $FeO+H_2=Fe+H_2O$, and $Fe_3O_4+H_2=3FeO+H_2O$ have been determined between about 657° and 1,025°; and a series of measurements has been made of the constant of the divariant equilibrium, $Fe_3O_4+CO=3FeO+CO_2$, between 816° and 1,039°. From the values obtained for the equilibrium constants, the equilibrium constant of the water gas reaction has been calculated. The values of I in the free-energy equation, calculated from the values of this constant, show a satisfactory constancy. Corrections to the free-energy data relating to CO and CO_2 have been made on the basis of the new results.

Eastwood, A. H. *See* abs. 1742.

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

764. Echard, —. [Petroleum Industry and Chemical Industry. Evolution in Germany.] Bull. assoc. franç. techniciens pétrole, No. 62, 1947, pp. 23–46; Chem. Abs., vol. 41, 1947, p. 7082.

Review of German developments in the utilization of paraffins and olefins as raw materials for the manufacture of synthetic lubricants, plasticizers, detergents, fatty acids, and alcohols (Oxo process).

765. Eckell, J. [Relations Between Structure of Catalyst and Chemical Change. I.] Ztschr. Elektrochem., vol. 39, 1933, pp. 423–432; Chem. Abs., vol. 27, 1933, p. 4996.

Historical review of previous work on this problem, with many refs.

766. ———. [Relations Between Structure of Catalyst and Chemical Change. II.] Ztschr. Elektrochem., vol. 39, 1933, pp. 433–439; Chem. Abs., vol. 27, 1933, p. 4996.

Effect of cold working on the catalytic activity of Ni foil used in the hydrogenation of C_2H_4 was studied. After the foil was rolled to a thickness of 0.1 mm., the strip was divided into 2 sections; 1 section was tested for catalytic activity without further treatment while the other was recrystallized by heating for 5 hr. in a high vacuum at 900°. The recrystallized strip was always inactive. The untreated strip decreased in activity after the 1st run. The recrystallized strip after being polished became as active as the untreated cold-rolled strip. The catalytic action was independent of the size of the surface area but depended on the structure. The activity of the Ni is attributed to deformation of the space lattice of the surface crystals by cold rolling or polishing.

767. Eckstrom, H. C., and Adcock, W. A. New Iron Carbide in Hydrocarbon-Synthesis Catalysts. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1042–1043.

During the course of hydrocarbon-synthesis investigations, X-ray diffraction patterns of certain catalyst samples have indicated the presence of a new Fe carbide phase. The new carbide appeared along with Fe_3O_4 and Fe_2C (Hägg) during a fluidized synthesis run at 27 atm. pressure and 360°, and eventually it constituted approximately 90% of the total catalyst charge. The X-ray diffraction pattern is shown in comparison with those of Fe_3O_4 and Fe_2C (Hägg). The *d/n* values and relative line intensities are given also. The new carbide is ferromagnetic; and, within the limits of experimental error, its Curie temperature is the same as that of Fe_2C (Hägg), (250°+ or −3°). After heating the sample for 10 min. at 600°, an X-ray diffraction pattern showed that the carbide had been converted partly to cementite, Fe_3C; after 30 min., all the carbide had been converted into Fe_3C. A chemical analysis gave 77.4% Fe and 17.4% C. This gives an Fe : C ratio of 0.96, so that the new phase could be equivalent to FeC.

Edeburn, P. W. *See* abs. 3150, 3151, 3152.

768. Edeburn, P. W., Schmidt, L. D., McGee, J. P., and Bonar, F. Pulverized Fuel Process for Synthesis-Gas Experimental Unit Operating on Entrained Powder. Am. Chem. Soc., 112th Meeting, Symposium on Production of Synthesis Gas, September 1947, pp. 123–136.

Description of an experimental unit designed for the dual purpose of obtaining data for the design and construction of a large-scale unit to develop a new process using entrained powder for making synthesis gas from pulverized fuel, and for testing cokes, chars, and coal from various sources for their synthesis-gas-making properties. A literature investigation disclosed that reactivity tests would not give the desired information because of the narrow reactivity range of solid fuels at gas-making temperatures. The apparatus as designed includes a generator and a purification train. The heat insulated reaction chamber of the generator is a 3-inch-i. d. refractory tube 4 ft. long placed inside a concentric 6-inch tube of the same material, the latter extending 6 in. below the lower end of the inner tube. The reacting materials and the flames for heating pass down the inner tube and then up the annular space between the tubes and out at the top to the purification train. A novel and simple O_2 : steam ratio controller is described. Data obtained in 2 initial runs are included.

Edwin, B. *See* abs. 161.

Egleson, G. C. *See* abs. 3023.

769. Egloff, G. [Modern Hydrocarbon Syntheses.] Brennstoff-Chem., vol. 18, 1937, pp. 115–117; Chem. Abs., vol. 31, 1937, p. 4789.

Brief account of production of high-octane motor fuels by cracking petroleum, Fischer's Kogasin, etc., and by the polymerization of gaseous olefins.

770. ———. Manufacture and Use of Substitute Motor Fuels Is Proving Costly in Europe. Oil Gas Jour., vol. 37, No. 17, 1938, pp. 56, 58–59, 62–64, 67.

In 1937, consumption of substitutes composed of synthetic gasoline and benzol from coal, alcohol, and oil shale amounted to about 18% of the total gasoline consumption. Gives retail prices, import duty, and taxes on motor fuel in principal cities in Europe.

771. ———. Motor-Fuel Economy of Europe. Ind. Eng. Chem., vol. 30, 1938, pp. 1091–1104; Chem. Abs., vol. 33, 1939, p. 343.

Coal is converted into liquid motor fuel by carbonization, hydrogenation, and the water-gas reaction. Alcohols from farm products and MeOH from hydrogenation of CO and from wood distillation also are used. CH_4, C_2H_6, C_3H_8, butanes, and city gas are used in compressed form in steel cylinders (3,000–4,000 p. s. i. pressure) in gas-driven motor vehicles. These

gases are derived from coal carbonization, coal hydrogenation, and from hydrogenation of CO and natural gas. There are about 26,000 of this type of motor vehicles in use. Other types of gas-driven vehicles manufacture their own combustible gas en route from wood and charcoal. There are about 9,000 such motor vehicles in Europe consuming about 450,000,000 lb. of wood yearly. These vehicles are heavily subsidized by governments by direct payments, elimination of taxes on the wood and vehicle, and taxes on imported gasoline. Total consumption of power alcohol in Europe in 1937 amounted to 510,000 tons compared with 646,000 tons during 1936. The 510,000 tons of EtOH (some MeOH) represented 4.3% of the total 11,882,600 metric tons of motor fuel consumed during 1937 in Europe. It is estimated that the 510,000 tons of alcohol used in Europe cost the consumer and state in additional expenditures on the order of about $100,000,000 in subsidies, tax losses, and higher operating costs of vehicles. Figures on the cost of production of gasoline from coal hydrogenation or from water gas are taken from the reports of the Committee of Imperial Defense (Falmouth Committee) and the Labor Party; from coal hydrogenation, $0.156 and $0.183 per gal., and from synthesis, from CO, $0.217 and $0.21 per gal.

772. ———. Motor Fuels of the Present and Future. Jour. Inst. Fuel, vol. 13, 1940, pp. 175–188; Chem. Abs., vol. 34, 1940, p. 8233.

Reviews source and characteristics of various natural and synthetic motor fuels

773. ———. Petroleum Looks Ahead. Chem. and Eng. News, vol. 23, No. 11, 1945, p. 987.

This address was given before the 10th annual petroleum meeting of the Wichita section, Am. Chem. Soc. Development work on the production of gasoline by coal hydrogenation is commendable for use, but requires 4 tons of coal per ton of gasoline produced. It is a costly operation. There are greater potentialities in the hydrogenation of shale oil of which there are large reserves. The Fischer-Tropsch process is probably the most versatile reaction known, with capabilities of producing many oxidized compounds, alcohols, diesel fuel, and other products.

774. ———. Fuel Developments in Midwest. Chem. Eng., vol. 55, No. 9, 1948, pp. 142–144.

Brief review of current developments in catalytic cracking of petroleum, synthesis of oil from natural gas, coal burning and gasification, and oil from coal by hydrogenation.

———. *See* abs. 204, 2164, 2326.

775. Egloff, G., and Van Arsdell, P. M. Substitute Fuels as a War Economy. Jour. Inst. Petrol., vol. 28, 1942, pp. 115–132.

Fischer-Tropsch plants in Germany [1]

Plant	Date placed in operation	1938	Production, bbl, 1939	1940
Schwarzheide	1937			
Wanne Eickel	1939		425,000	1,700,000
Bochum	1939		425,000	1,700,000
Rauxel	1938	340,000	425,000	1,700,000
Sterkrade-Holten	1938	255,000	637,500	850,000
Moers-Moerbeck	1936 and 1939	255,000	765,000	765,000
Koln Neussen	1938	255,000	425,000	425,000
Dortmund	1939			
Deschowitz	1939		212,500	425,000
Essen	1938 and 1939	212,500	425,000	1,870,000
Essen	1939	255,000	425,000	425,000
Recklinghausen [2]	1936	850,000	1,062,500	1,275,000
Total		2,422,500	5,227,500	11,135,000

[1] From La Revue pétrolifère, 1941, p. 237.

[2] Intern. Hydrogenation Patents Process.

These data are incomplete as to the actual number of plants operating.

776. Egloff, G., Nelson, E. F., and Morrell, J. C. Motor Fuel From Oil Cracking-Production by the Catalytic Water-Gas Reaction. Ind. Eng. Chem., vol. 29, 1937, pp. 555–559; Brennstoff-Chem. vol. 18, 1937, pp. 260–263; Chem Abs., vol. 31, 1937, pp. 4482.

Synthetic gasoline produced by the Kogasin process is claimed to be produced in 81.6% yield and is principally a straight-chain or slightly branched-chain mixture of saturated and unsaturated hydrocarbons, having the fractions: gasoline, 30°–220°; diesel oil, 220°–350°; and wax separated from the diesel-oil fraction. The gasoline fraction is water-white and S-free, and olefins are present to over 50%. The octane number is below 50. Experiments are reported on the reforming of this naphtha and cracking the bottoms from the distillation operation. The final gasoline product, obtained by blending the low-boiling products from the topping and cracking with a high antiknock gasoline that is obtained by catalytically polymerizing the olefinic gases obtained by cracking, had an octane value of 66, which could readily be increased by more drastic cracking. The possibility of producing a good aviation gasoline by blending low-boiling straight-run with the polymer gasoline is indicated.

777. Eguchi, T. Synthesis of Methanol From Coal. Fuel Econ., vol. 11, 1936, pp. 417–420; Trans. World Power Conf., 3d Chem. Eng. Cong., London, 1936; Chem. Zentralb., 1936, II, p. 3467; Chem. Abs., vol. 30, 1936, p. 7816.

With reduced Cu as catalyst, 87% of the gas $CO+H_2$ is converted to CH_3OH at 250° and 100 atm. S compounds, hydrocarbons of the C_2H_2 series, and gaseous Fe-group compounds are poisonous to Cu oxide catalysts but have less effect on Zn oxide catalysts. A special catalyst operating at 230° and 100 atm. has been in use over a month with but slight decrease in CH_3OH yield. The gas is obtained directly from a gas generator with coal as a raw material.

778. Ehrhardt, U. [Literature Survey on the Synthetic Production of Mineral Oils From Gases.] Ges. Abhandl. Kenntnis Kohle, vol. 4, 1919, pp. 471–506.

Ehrmann, —. *See* abs. 2264, 2265.

Eichner, C. *See* abs. 2743, 2744.

779. Eichner, C., Perrin, M., and Prettre, M. [Controlled Catalytic Combustion of Methane.] Compt. rend., vol. 218, 1944, pp. 621–623; Bull. soc. chim., 1944, p. 388; Chem. Abs., vol. 40, 1946, p. 1643.

With a limited O_2 supply, possible reactions are: (1) $2CH_4+O_2=2CO+4H_2$; (2) $CH_4+2O_2=CO_2+2H_2O$; (3) $2CH_4+3O_2=2CO+4H_2O$; (4) $CH_4+O_2=CO_2+2H_2$; residual CH_4 and reaction products may give (5) $CH_4+H_2O=CO+3H_2$ and (6) $CO+H_2O=CO_2+H_2$, 2 independent reactions. A mixture of O_2 and CH_4 entering a catalytic column previously brought to constant temperature produces an initial rise followed by a drop in temperature; this indicates at least 2 steps to the reaction; only (5) is endothermic. Equilibria (1) and (5) give very poor yields below 1,000°. Composition of gases after reaction indicates (4) does not occur. Calculated and experimental results for equilibria (5) and (6) compare well at 725°–870°. When equilibrium is not attained, analyses show (2) to be the preferred mechanism; an excess of H_2O and CO_2 is found in the gas mixture leaving the column; (3) sometimes occurs.

780. Eidus, Y. T. [Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Uspekhi Khim., vol. 7, 1938, pp. 1714–1754 and 1801–1857; Chem. Zentralb., 1939, II, p. 359.

Comprehensive review.

781. ———. [Mechanism of the Synthesis of Aliphatic Hydrocarbons by the Contact Hydrogenation of Carbon Monoxide.] Uspekhi Khim., vol. 9, 1940, pp. 673–681; Chem. Abs., vol. 35, 1941, p. 1023.

Carbide theory in connection with Co catalysts is explained, and photochemical data are cited on the nature of the CO bonds. (*See also* abs. 780.)

782. ———. Reactions of Some Oxygen-Containing Organic Compounds Over the Cobalt Contact Catalysts Used for the Synthesis of Gasoline From Water Gas. Bull. acad. sci. U. R. S. S., classe sci. chim., 1943, pp. 65–73 (English summary); Nat. Petrol. News, vol. 37, No. 14, 1945, pp. R–302, 304, 306; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 439; Chem. Abs., vol. 38, 1944, p. 1342.

MeOH decomposes almost completely over a Co–ThO_2–kieselguhr catalyst at 170°–200°, forming CO and H_2. These react further to form a mixture of liquid hydrocarbons similar in properties to, but smaller in amount than, the mixture obtained directly from water gas over this catalyst. HCO_2H similarly decomposes, chiefly to H_2 and CO_2, somewhat less to H_2O and CO, and very slightly to HCHO, CO_2, and H_2O. EtOH gives a series of products, of which the chief are CH_4, CO, and H_2. In both cases liquid hydrocarbons are formed, but always as secondary products from CO and H_2. Thus, MeOH, HCO_2H, and EtOH cannot be intermediates in the synthesis of hydrocarbons from water gas.

783. ———. [Catalysts for Hydrogenation of Carbon Monoxide by Joint Application of the Dynamic and Static Methods. I. Activity of the Complex Fe-Cu-ThO_2-K_2CO_3-Kieselguhr Catalyst.] Bull. acad. sc. U. R. S. S., classe sci. chim., 1944, pp. 255–262; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 492A; Chem. Abs., vol. 39, 1945, p. 2391.

Reaction was studied in a current of gas and also, by rate of change of pressure, in a closed system. On Fe-type catalysts, in contrast to the Co-type catalysts, the intermediate step in the synthesis is the formation of carbides. The change in the activity of the catalyst Fe–Cu–ThO_2–K_2CO_3–kieselguhr at the different moments of the contact process of formation of hydrocarbons from CO_2 and H_2 was studied by simultaneous application of the dynamic and static methods; the reaction of this contact mass to H_2, CO, and CO_2 separately and to water gas with addition of CO was also investigated.

784. EIDUS, Y. T., AND ALTSHULLER, S. B. [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Use of the Dynamic and Static Methods. II. Activity of Catalysts Containing Various Components of the Catalyst Fe–Cu–ThO_2–K_2CO_3–Kieselguhr.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1944, pp. 249–357; U. O. P. Co. Survey Foreign Petroleum Literature Transl., May 1945, No. 507; Chem. Abs., vol. 39, 1945, p. 3142.

12 Catalysts containing varying combinations of the components of the complex catalyst Fe–Cu–ThO_2–K_2CO_3–kieselguhr made up in proportion of 100:25:2:2:125 have been investigated by a combined method with respect to their activity in hydrogenation of CO and interaction of CO with the catalytic surface at 258°. It was established that only those catalysts that contain both Fe and Cu as well as one of the promoters, either ThO_2 or K_2CO_3, are active in the process discussed. However, addition of the 2d promoter brings about a sharp rise in the activity of the catalyst. In both processes studied, the change in the initial velocity of the process is well correlated with the composition of the catalyst. These data, in conjunction with those previously reported (abs. 783) justify an assumption that synthesis of hydrocarbons from CO and H_2, over Fe catalysts, involves carbide formation as an intermediate step, which does not take place over Co or Ni catalysts. The dependence of the velocity of the total process of hydrogenation of CO to hydrocarbons on the Fe–Cu–ThO_2–K_2CO_3–kieselguhr catalyst in the above proportions upon the temperature was studied in a static system. The apparent energy of activation within 245° and 265° was found to amount to 28.7 calories per mole. The pre-exponential member of the Arrhenius equation is diminished at temperatures above 255°, which may be due to formation of new reaction products resulting in a decrease of the number of active centers on the surface of the catalyst that participate in the basic reaction.

785. EIDUS, Y. T. [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Application of the Dynamic and Static Methods. III. The Part Played by the Alkaline Activator in the Formation of the Surface of the Catalyst Fe–Cu–ThO_2–K_2CO_3–Kieselguhr.] Bull. acad. sci. U. R. S. S., classe sci. chim., No. 1, 1945, pp. 62–70; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 537; Chem. Abs., vol. 39, 1945, p. 4792.

Catalyst Fe–Cu–ThO_2–K_2CO_3–kieselguhr, composed in the proportion of 100:25:2:2:125, was investigated for the reaction of hydrogenation of CO_2; 4 catalysts made up of various components of this catalyst were likewise studied for their interaction with CO_2 at 258°. It was found that no catalytic hydrogenation of CO_2 takes place under the conditions used. Data were obtained showing that the interaction of CO_2 with the surface of the catalyst is due to K_2CO_3 and that addition of ThO_2 promotes this process. The alkaline activating agent, while contained in only slight amount in the catalyst, accumulates on the surface of the latter and occupies a substantial portion of its active part. The accumulation of the activator on the surface of the catalyst is the cause of the activity of the latter with respect to carbide formation, hydrogenation of CO and interaction of CO_2 with the catalytic surface.

786. ———. [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Application of the Dynamic and Static Methods. IV. Kinetics of Carbide Formation and of Hydrogenation of Carbon Monoxide on Co, Ni, and Fe Catalysts.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1946, pp. 447–453; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 656, 1946, 7 pp.; Chem. Abs., vol. 43, 1949, p. 6063.

By the simultaneous application of the dynamic and static methods, a comparative study was carried out of the kinetics of hydrogenation of CO and of the interaction of the latter with the surface of Co–Th–marshallite catalysts (100 : 18 : 100), of Ni–Mn–Al–marshallite (100:20:10:100), and of Fe–Cu–Th–K_2CO_3–marshallite (100 : 25 : 2 : 2 : 125). With the Co and Ni catalysts, the reaction temperatures were 180°–210° with a gas mixture 1 CO : 2 H_2; in the case of Fe catalyst, 230°–260° and 1 CO : 1 H_2. The carbide formation and the hydrogenation of CO were studied at identical temperatures in the same catalytic furnace. The kinetic data obtained show that the ratio of the initial velocities of hydrogenation of CO to the carbide formation is much lower in the case of the Fe catalyst than for the Co and Ni catalysts. The lower ratio for the Fe catalyst results from the reduced hydrogenation velocity of CO on this catalyst as compared with the velocity of this process on the Co and Ni catalysts. This is in agreement with the carbide theory of synthesis of hydrocarbons from CO and H_2. On Co and Ni catalysts, the rate of hydrogenation of CO materially exceeds that of interaction of CO with the catalyst, which contradicts the carbide theory of catalytic synthesis of hydrocarbons from CO and H_2 on these catalysts. If formation of liquid and solid hydrocarbons by hydrogenation of CO involves the carbide mechanism

$$\begin{array}{ll}(1) & 2CO \rightarrow CO_2 + C(\text{carbide}) \quad (a) \\[6pt] (2) & \dfrac{C(\text{carbide}) + H_2 \rightarrow CH_2 \quad (b)}{2CO + H_2 \rightarrow CO_2 + \underset{\substack{\downarrow \\ (CH_2)_n}}{CH_2} \quad (c)}\end{array}$$

then the conclusion can be drawn from the experimental data obtained that equality of the reaction velocities of (*a*) and (*c*) is in accord with the carbide theory only in the case of Fe catalysts; for the Co and Ni catalysts, the velocity of the process is considerably in excess of that in the process (*a*). All this speaks against the applicability of the carbide-formation mechanism for the explanation of the chemical process occurring on the Co and Ni catalysts and in favor of this mechanism of synthesis of hydrocarbons from CO and H_2 in the case of Fe catalysts. This is also supported by data previously reported by the author.

787. ———. [Reduction of Catalysts for the Synthesis of Aliphatic Hydrocarbons From Mixtures of Carbon Monoxide and Hydrogen.] Jour. Gen. Chem. (U. S. S. R.), vol. 16, 1946, pp. 875–883; Chem. Abs., vol. 41, 1947, p. 1824.

A comparative study was made on reduction of the following water-gas catalysts: Co–ThO_2–kieselguhr (100 : 18 : 100), Fe–Cu–ThO_2–K_2CO_3–kieselguhr (100 : 25:2:2:125), and Fe–Cu–ThO_2–K_2CO_3–marshallite (100;25:2:2:125). The general course of reduction was similar in both catalyst types, with the maximum reduction rate occurring at the beginning of reduction. Reduction with H_2 at 375° proceeds more rapidly and results in twice as great a loss in weight in the 1st catalyst as was observed for the 2d and 3d catalysts at 250°; the latter catalysts are reducible with H_2 only to the extent of 82%. Interaction of these catalysts with CO first results in further reduction of the former (loss in weight) followed by carbide formation (weight gain). CO is adsorbed on the 1st catalyst 4 times more effectively than on the 2d or 3d, after H_2 reduction. Slow heating-up of the latter catalysts during H_2 reduction gives the most active catalysts.

788. ———. [Synthesis of Liquid and Solid Hydrocarbons from Water Gas at Atmospheric Pressure on a Precipitated Fe–Cu–ThO_2–K_2CO_3–Marshallite Catalyst.] Jour. Gen. Chem. (U. S. S. R.), vol. 16, 1946, pp. 869–874; Chem. Abs., vol. 41, 1947, p. 1987.

Precipitated Fe–Cu–ThO_2–K_2CO_3–marshallite catalyst was shown to have a rather high effectiveness in the synthesis of hydrocarbons from water gas at 250° and atmospheric pressure. The best catalyst contained a 1: 2 ratio of ThO_2 : K_2CO_3, which was used in 2% amount relative to Fe. Yields of solid paraffins as high as 13.6% are reported.

789. ———. [Progress in the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Uspekhi Khim., vol. 19, 1950, pp. 32–58; Chem. Zentralb., 1950, II, p. 1173.

Summary of progress during the last 10 yr. Following points are discussed: (1) Role of the various components in the catalysts of CO–H_2 synthesis; (2) precipitation of Co–Ni catalysts; (3) Fe catalysts; (4) Ru catalysts; (5) technical Co catalyst; (6) synthesis in the liquid phase; (7) the decline in catalyst activity; (8) isosynthesis; (9) synthesis of aromatics; (10) Synol process; (11) Oxo synthesis; (12) hydrocondensation of Co, H_2, and olefins (pressureless). 121 literature refs.

789a. ———. [Mechanism of Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] Uspekhi Khim., vol. 20, 1951, pp. 54–70; Chem. Zentralb., 152, I, p. 3430.

Following subjects are discussed: Carbide formation, carbide formation as the intermediate step in the synthesis, oxygenated compounds as the intermediate step and methylene radicals as the intermediate step. 90 literature refs.

———. [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Application of the Dynamic and Static Methods. III. Part Played by the Alkaline Activator in the Formation of the Surface of the Catalyst Iron-Copper-Thoria-Potassium Carbonate-Kieselguhr.] *See* abs. 785.

———. [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Application of the Dynamic and Static Methods. IV. Kinetics of Carbide Formation and of Hydrogenation of Carbon Monoxide on Cobalt, Nickel, and Iron Catalysts.] *See* abs. 786.

———. *See* abs. 802a.

EIDUS, Y. T., AND ALTSHULLER, S. B. [Investigation of Catalysts for Hydrogenation of Carbon Monoxide by Simultaneous Use of the Dynamic and Static Methods. II. Activity of Catalysts Containing Various Components of the Catalyst Iron–Copper–Thorium Dioxide–Potassium Carbonate–Kieselguhr.] *See* abs. 784.

790. EIDUS, Y. T., AND ELAGINA, N. V. Activity and Stability of Fe–Cu–ThO_2–K_2CO_3 Catalyst in the Synthesis of Liquid Hydrocarbons From CO–H_2 Mixture as Influenced by Composition of the Catalyst and the Nature of the Carrier. Bull. acad. sci. U. R. S. S., classe sci. chim., 1943, pp. 305–311 (English summary); U. O. P. Co. Survey Foreign Petroleum Literature Transl. 468; Chem. Abs., vol. 38, 1944, p. 5648.

18 catalysts of composition Fe–Cu–ThO_2–K_2CO_3–carrier were examined in the synthesis of liquid hydrocarbons from 1 CO : 2H_2 mixture. The catalyst Fe 100 : Cu 25 : K_2CO_3 2 : kieselguhr 125 shows a sharp optimum for ThO_2 content at 1%. Slight maximum in efficiency is found at 2% K_2CO_3 in Fe 100 : Cu 25 : ThO_2–kieselguhr catalyst. In this catalyst, the best results were obtained with the carrier of Insen diatomite and marshallite, the latter support being somewhat more stable. The results contradict the view of catalyst support as an inert mass. The Fe catalysts investigated showed poor stability, which was not improved with variations of ThO_2 content.

791. EIDUS, Y. T., AND GUSEVA, I. V. [Effect of Ammonia in the Incoming Gas on the Catalytic Hydrogenation of Carbon Monoxide to Higher Hydrocarbons.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1950, pp. 287–290; Chem. Abs., vol. 44, 1950, p. 8087.

In 5-hr. runs with a mixture of 1 CO : 2 H_2 flowing at 80–90 l. per l. catalyst per hr. at 190° and atmospheric pressure over a Co catalyst (5 gm. metal over 35 cm.), addition of NH_3 resulted in marked decrease of the yield of higher hydrocarbons without any increase in the amount of CH_4; the % of CO reacted is decreased in the same degree as the yield of hydrocarbons. A precipitate of $(NH_4)_2CO_3$ is formed at the end of the reactor. The effect of NH_3 is reversible; as soon as the NH_3 is shut off, the yield reverts to its original high level. Judging by the absence of $MeNH_2$ (also of Me_2NH, Me_3N, and $CO(NH_2)_2$) in the products, the inhibition by NH_3 is not due to a reaction $NH_3 + CH_2 \rightarrow MeNH_2$. The formation of $(NH_4)_2CO_3$ can be attributed only to enhanced occurrence of the reaction $CO + H_2O \rightarrow CO_2 + H_2$, with CO_2 reacting further with NH_3; in the absence of NH_3, that reaction ordinarily ceases as soon as the catalyst is formed, but not with NH_3 present.

792. Eidus, Y. T., and Puzitskii, K. V. Catalytic Hydrocondensation of Carbon Monoxide With Ethylene. Compt. rend. acad. sci. U. R. S. S., vol. 54, 1946, pp. 35–38 (in English); Chem. Abs., vol. 41, 1947, p. 3741.

Using the same method of preparation as described previously (Eidus and Zelinskii, abs. 793), but using Co(I) and Co(II), differing in preparation, as catalysts, the catalytic interaction of C_2H_4 with CO in the presence of H_2 at 760 mm. pressure was studied. (I) was not stable enough; (II) was more stable. Results show that a hydrocondensation reaction of CO with C_2H_4 in the presence of H_2 takes place; 75% by volume of liquid product is formed at the expense of the initial C_2H_4. The presence of a considerable amount of O_2-containing compounds was detected, particularly alcohols. PrOH was detected as the 3-nitrophthalate.

793. Eidus, Y. T., and Zelinskiĭ, N. D. [Intermediate Formation of Methylene Radicals During the Catalytic Synthesis of Aliphatic Hydrocarbons From Carbon Monoxide and Hydrogen.] Bull. acad. sci. U. R. S. S., classe sci. chim. 1940, pp. 289–293; Chem. Abs., vol. 35, 1941, p. 4744.

A very highly purified mixture of CO and H_2 (1 : 2) was allowed to react over a Ni–Co–Al catalyst in the presence of C_6H_6(I) at 190°: small quantities of toluene (II) and xylene (?) were formed (detected as nitrotoluene and nitroxylene (?), respectively). The formation of (II) was explained through the action upon (I) of methylene radicals, intermediately formed during the contact hydrogenation of CO.

794. ———. [Carbide Formation as an Intermediate Stage in the Catalytic Synthesis of Hydrocarbons From Water Gas.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1942, pp. 190–194; U. O. P. Co. Survey Foreign Petroleum Literature Transl. No. 385; Chem. Abs., vol. 39, 1945, p. 2391.

The Co carbide formed by the action of CO on the Co–ThO_2–kieselguhr catalyst is neither an intermediate product nor a catalyst of the synthesis of gasoline from CO and H_2. Intermediate formation of methylene radicals during this synthesis appears to be confirmed.

795. ———. [Reaction of Carbon Monoxide With Cobalt Catalysts Used in the Synthesis of Gasoline From Water Gas.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1942, pp. 45–54; Chem. Zentralb., 1943, II, p. 1770; Chem. Abs., vol. 37, 1943, p. 2909.

When CO is passed over a mixture of 100 parts Co, 18 parts ThO_2, and 100 parts kieselguhr at 192°–272°, 2 reactions occur, forming, respectively, Co_2C and C. At 192°–212°, a carbide formation predominates; but, as the temperature rises, more free C is formed, and at 272°, 5 gm.-atoms C form per gm. atom Co. At this temperature, decomposition of Co_2C also occurs. Poisoning of the catalyst with SO_2 also reduces Co_2C formation. Reduction of Co_2C by H_2 goes faster and at a lower temperature on this catalyst than on pure Co.

796. Eidus, Y. T., Elagina, N. V., and Zelinskiĭ, N. D. [Synthesis of Olefin Hydrocarbons From Primary Alkyl Magnesium Halides and Carbon Monoxide Under Pressure.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1945, pp. 672–674; Chem. Abs., vol. 42, 1948, p. 5838.

Effect of changing the halide in 2 examples of Fischer and Stoffers's reaction between Grignard reagents and CO under pressure is studied. The substitution of BuMgBr and iso–AmMgCl for BuMgCl and iso–AmMgBr yields the same products, 4–nonene and 2–8–dimethyl–4–nonene, respectively, but the yields are 25.4% and 51% instead of 51% and 53.6%, respectively.

797. Eidus, Y. T., Kazanskii, B. A. and Zelinskiĭ, N. D. [Influence of the Type of Carrier on the Synthesis of Liquid Hydrocarbons Over Ni–MnO–Al_2O_3 Catalysts at Atmospheric Pressure.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1941, pp. 27–33; Chem. Zentralb., 1942, II, p. 642; U. O. P. Co. Survey Foreign Petroleum Literature Transl. No. 325–B; Chem. Abs., vol. 37, 1943, p. 5306.

Effect of using supports of kieselguhr from different parts of Russia for the (5 Ni+Mn)+10% Al_2O_3 catalyst used in preparing hydrocarbons from CO and H_2 is reported. The degree of washing the catalyst after precipitation has great influence on its activity, and the separation of Fe and ignition are not always required.

798. Eidus, Y. T., Zelinskiĭ, N. D., and Ershov, N. I. [Condensing Action of Methylene Radicals on Ethylene.] Compt. rend. acad. sci. U. R. S. S., vol. 60, 1948, pp. 599–601; Chem. Abs., vol. 43, 1949, p. 108.

In hydropolymerization of C_2H_4, the most important role is played by the CH_2 radicals. Using, as a source of CH_2 radicals, molecules of CO in the course of hydrogenation, a new reaction of catalytic hydropolymerization of C_2H_4 was discovered, which proceeds only in the presence of small amounts of CO. With an equimolecular mixture of C_2H_4 and H_2, containing 4–7% CO, and a space velocity 100 at 190° at atmospheric pressure, intensive hydropolymerization takes place on the catalyst surface; selection of the conditions may restrict hydrogenation of C_2H_4 to 25–30% of the total reaction. The yields of liquid hydrocarbons reach 400–500 ml. per $m.^3$ or 30–45 ml. per hr. Distillation of a typical run showed the presence of 54% butylene, 4.1% butane, 19% propylene, 3.3% propane, 18.2% ethane, and 1.1% C_2H_4, in addition to which appreciable amounts (up to 60–65%) of C_5–C_8 hydrocarbons are formed. Increase of the CO content 0.06–6.1% increases the amount of heavy oil (in ml. per $m.^3$) 0–61.3. The light oil reaches a maximum of 193.5 ml. per $m.^3$ at 4% CO, while gas oil (C_4 and lower) reaches a maximum of 153.9 ml. per $m.^3$ at 1.5% CO. Complete absence of CO led to the failure of formation of any higher oil; only hydrogenation to C_2H_6 took place.

799. Eidus, Y. T., Zelinskiĭ, N. D. and Puzitskiĭ, K. V. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. I. Hydrocondensation of Carbon Monoxide With Ethylene.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1949, pp. 110–114; Associated Tech. Services, Transl. RF–24, April 1950; Chem. Abs., vol. 43, 1949, p. 4829.

Mixtures of CO, H_2, and C_2H_4 passed over a catalyst under atmospheric pressure at 190°–200° undergo hydrocondensation, mainly into aliphatic hydrocarbons. The following data give the composition of the gaseous mixture, space velocity in l. per l. catalyst per hr., duration in hours, yields (in mil. per $m.^3$ of total gas passed) of heavy oil, light oil, total oil, H_2O; mean yield of total oil in ml. per l. catalyst per hr.: 1 CO : $2H_2$: $3C_2H_4$, 93, 90, 130.8, 212.5, 343.3, 29.6, 30.2; 1 CO : $2H_2$: $1.5C_2H_4$, 106, 71, 107.5, 88.1, 195.6, 19.4, 85.1. On a particularly active catalyst, a mixture 1 CO : $2H_2$: $3C_2H_4$ gave, at a space velocity of 114–135, in 49 hr., total oil 333–465 ml. per $m.^3$ total gas passed, or 33–49 ml. oil per l. catalyst per hr., with a maximum of 465.2 ml. per $m.^3$ or 49.2 ml. per l. per hr., at a space velocity of 118. The yield of H_2O was 55–96 ml. per $m.^3$, and the volume ratio of light to heavy oil decreased during the operation from 1.42 to 0.85. The balance of the C_2H_6 formed and of the amounts of each component spent in the reaction shows that C_2H_4 reacts to the extent of 80–93% and that only 15–22% of the C_2H_4 that reacts is spent on formation of C_2H_6; H_2 reacts to the extent of 87–99%, with only 20–33% of the reacting H_2 being spent on formation of C_2H_6. Of the CO, 71.4% enters the reaction at its initial stage; at later stages, about 48–51% of the CO enters the reaction. Formation of the liquid and solid products consumes, on the average, 2–3 vol. H_2 and 3–4.5 vol. C_2H_4 per vol. CO. Preliminary study of the oily and aqueous products showed only a small amount of oxygenated compounds, mainly alcohols; among these, iso–PrOH was identified. The oil is a mixture of saturated and unsaturated aliphatic hydrocarbons.

800. ———. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. II. Liquid Products of Hydrocondensation of Carbon Monoxide With Ethylene.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1949, pp. 326–332. Chem. Abs., vol. 44, 1950, p. 4409.

Hydrocondensation of CO–3 C_2H_4–2 H_2 at 190° yields the oil layer, which was separated into components conventionally. These comprised 2–3% O_2 derivatives (10% in the aqueous layer of catalyzate). The aldehyde content was 0.9% in the oil and 1.9% in the aqueous layer. Of these only EtCHO was identified. Ketones are absent. The aqueous layer contained 1.5% organic acids, of which 70% was EtCOOH. The hydrocarbons formed in the reaction represent a very wide boiling range and are a complex mixture of paraffins and olefins containing C_6, C_5, C_5. and C_7 members: the latter probably form by intermediacy of CH_2 radicals, which are believed to be the principal hydrocarbon-forming agency. The nonparticipation of CO in this reaction is confirmed by lack of condensation of CO with C_2H_4 in the absence of H_2. Small amounts of PrOH were isolated from the summary reaction product (identified as the 3–nitrophthalate).

801. ———. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. III. Polymerization and Hydropolymerization of Ethylene Under the Conditions of Hydrocondensation Catalysis.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1950, pp. 98–107; Chem. Abs., vol. 44, 1950, p. 6100.

(1) C_2H_4 alone and in mixture with H_2 was passed at 190°, under atmospheric pressure, over catalyst (III) after it had been used for 120 hr. in hydrocondensation of $1CO:2H_2:3C_2H_4$. Its activity in that reaction is expressed by the production of 218–237 ml. per $m.^3$ oil, or 21.1 ml. per l. per hr. at space velocity $S=101$–114; gas contraction, $c=31.3\%$, H_2O yield, $w=20.8$–39.5 ml. per $m.^3$. In a subsequent run with C_2H_4 alone (86% pure), c was 12%, oil initially 62.7 ml. per $m.^3$ (6.0 ml. per l. per hr.), falling to 32.8 (2.9), extent of reaction 13% of the C_2H_4 passed, $w=15.7$–32.8 ml. per $m.^3$. This shows that, in $CO+H_2+C_2H_4$ the liquid products cannot be due to a polymerization of C_2H_4 itself. (2) In a subsequent run with $2C_2H_4:1H_2$, the oil yield rose to 118.2 ml. per $m.^3$ (9.7 ml. per l. per hr.), c to 32.2%, extent of reaction 46.7% of the C_2H_4 passed, with 53.7% of the C_2H_4 reacted spent on formation of liquid and solid products; H_2 reacted to the extent of 71.8%, with 34.1% of the H_2 reacted spent in the formation of liquid and solid. In a subsequent run with $1C_2H_4$: $1H_2$, the oil yield was 202.0 (20), c 48.3%, extent of reaction 87.7, and 72.7% of C_2H_4 and H_2 passed, respectively, with 45.4 and 28.5%, respectively, of the C_2H_4 and H_2 reacted gone into the liquid and solid product. In two following runs with $1C_2H_4:1.2H_2$, the C_2H_4 reacted completely (100%), but only 20–25% of it went into the oil the yield of which fell to 49.6 (3.5). The same results were obtained in an analogous series of runs, on catalyst (IV). As a rule, the proportion of light oil in the liquid product is markedly higher with $H_2+C_2H_4$ than with $CO+H_2+C_2H_4$ and increases in consecutive runs. (3) Passage of H_2 alone over a catalyst having been used in runs with $CO+H_2+C_2H_4$, produces no significant amounts of liquid and no light oil. This proves that the hydrocondensation products obtained with $H_2+C_2H_4$ are not due to a hydrogenation of the solid deposit formed on the surface of the catalyst. (4) Passage of $1H_2:1C_2H_4$ on a fresh catalyst produced practically no oil, only hydrocarbons C_4, with a yield of 5.2–14.0% with respect to C_2H_4 passed, or 35–90.5 liquid ml. (at −80°) per $m.^3$ gas passed. The main mass of the C_2H_4 is hydrogenated to C_2H_6. (5) These results are interpreted as being due to the presence of CH_2 radicals at certain points of the lattice of the metallic catalyst surface having been used with $CO+H_2+C_2H_4$. Wherever a CH_2 group happens to be located in a suitable position between the ends of 2 molecules of C_2H_4 adsorbed on the same surface, it serves as a bridge linking the C_2H_4 molecules and leading to the formation of higher polymerization products. Such CH_2 groups being absent at the surface of a fresh catalyst, the probability of higher polymerization is very slight and there can only be dimerization of adjacent C_2H_4 molecules into C_4 products.

802. Eidus, Y. T., Zelinskiĭ, N. D., Ershov, N. I., and Batuev, M. I. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. IV. Hydrocondensation of Ethylene With Carbon Monoxide at Low Concentrations of the Latter.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1950, pp. 377–385; Chem. Abs., vol. 45, 1951, p. 1495.

At 190° under atmospheric pressure, mixtures of C_2H_4 and H_2 with small amounts of CO gave with 3 different catalysts the following yields (vol. % C_2H_4, H_2, CO in the initial gas, space velocity, length of run in hours, yield (ml. per $m.^3$) of heavy oil, light oil, gas oil, and H_2O): 52.6, 37.5, 5.7, 104 l. per l. catalyst per hr., 12.2 hr., 86.3, 199.1, 285.4, 7.0; 48.9, 36.9, 7.6, 78, 47.0, 77.4, 224.8, 96.3, 21.3; 47.9, 38.5, 6.5, 85, 69.5, 38.7, 162.3, 100.4, 36.7. The composition of the outgoing gas (vol. %) in these 3 experiments was C_2H_4, H_2, CO, and C_2H_6, respectively: 2.4, 35.7, 0.8, 42.9; 19.1, 20.0, 9.7, 38.8; 12.8, 18.3, 8.6, 53.0 (balance N_2). The yield of liquid condensate (gas oil included) attains 30–45 ml. per l. per hr. C_2H_4 reacts to the extent of 77.7–98.5%, H_2 to 62.3–96.9%; CO is consumed mainly (up to 94.9%) in the beginning of the run, less at later stages. The fraction of the reacted C_2H_4 converted to C_2H_6 varies 27.6–56.6%. At constant space velocity, 100 l. per l. catalyst per hr., with a gas mixture containing about 7% CO, the optimum temperature, in the 100°–250° range, is 190°–210°. By fractionation of the products from an equimolecular mixture of C_2H_4 and H_2, containing 4–7% CO, the gas oil constitutes about 36% of all organic products in the condensate, and consists, in wt. % (not including CH_4) of C_2H_4, 1.1, C_2H_6, 18.2; C_3H_6, 19.0; C_3H_8, 3.3; C_4H_8, 54; C_4H_{10}, 4.1; or in % of the organic matter in the condensate, respectively, 0.35, 6.1, 6.3, 1.1, 18.1, 1.4. More than half of the gas oil, 54 wt. %, is the nonhydrogenated dimer of C_2H_4, namely C_4H_8; the hydrogenated dimer, C_4H_{10}, is 4.1% (with respect to the weight of the condensate, C_4H_8 is 18.1, C_4H_{10}, 1.4%). The presence of a $C_3H_8+C_3H_6$ fraction (22.3% of the gas oil, 7.4% of the condensate), with a C_3H_8 : C_3H_6 ratio of 0.2 : 0.3, indicates condensation of CH_2 radicals with C_2H_4. Fractions C_6 and C_8 (trimers and tetramers of C_2H_4) constitute, respectively, 18.8% and 12.6% of the condensate (with the gas oil separated); the presence of the fractions C_5, C_7, and C_9 constituting, respectively, 12%, 16.5%, and 8.5% of the gas oil-free condensate, indicates reaction with CH_2 radicals. Unsaturated compounds attain up to 70% of the condensate. By Raman spectra of the hydrogenated catalyzate, the fractions b. 69°–126.5° contain only the corresponding normal hydrocarbons, the fraction b. 66°–68.5°, beside C_6H_{14}, also contains about 15% 2-methylpentane and about 25% 3-methylpentane; the fraction b. 27°–36° contains, beside C_5H_{12}, about 15% 2-methylbutane.

802a. Zelinskiĭ, N. D., Eĭdus, Y. T., Puzitskiĭ, K. V., and Batuev, M. I. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. V. Hydrocondensation of Carbon Monoxide and Propylene.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1950, pp. 647–653; Chem. Abs., vol. 45, 1951, p. 8,437.

As shown earlier, in the complete absence of CO, C_2H_4 with H_2, under catalytic conditions, yields only C_2H_6, but in the presence of CO polymers and hydropolymers of odd and even number C atom hydrocarbons are formed. A similar reaction between propene and 5.7–7.0% CO at 190° and atmospheric pressure of H_2 with the previously described catalyst gives 85–90% conversion of the propene, of which 35% is C_3H_8; the yield of liquid condensate is 550–600 ml. per m.³. The yield of butylenes is 2.7%, that of C_4H_{10} 2.6%. The condensate freed of C_3 and C_4 products boils over a very wide range (30°–325°) and contains about 35% unsaturates, mostly of lower molecular weights. After hydrogenation over Raney Ni 75% of the condensate b. 28°–340°, and contains about 12–14% each of C_5, C_7, C_8, and C_9 products, about 20% C_6. The C_5–C_6 fractions contain some branched-chain products (Raman method), possibly 2- and 3-methylpentane, while the rest are *n*-hydrocarbons C_5–C_7.

802b. Eidus, Y. T., Ershov, N. I., Batuev, M. I., and Zelinskiĭ, N. D. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. VI. Hydrocondensation of Carbon Monoxide With *n*-Butylene.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1951, pp. 722–727; Jour. Inst. Petrol., vol. 38, 1952, p. 215A.

Experiments were carried out on equimolecular mixture of H_2 and C_4H_8+2.6–6% of CO, under the same conditions as previously. At 2.6% CO 100% of CO and 97.1% of C_4H_8 react, at 6% CO, 100%, and 70.4%, respectively. 30–35% of the C_4H_8 is reduced to C_4H_{10}. Liquid products, >C_4, have b. p. 28°–276° C. and consist of aliphatic hydrocarbons, unsaturates 28%. After hydrogenation liquid condensate was fractionated; analysis (Raman spectra) showed 24% C_5 (about half of which is isopentane), 15% C_6, 8% C_7, 8% C_8, 9% C_9, as well as higher hydrocarbons.

802c. Eidus, Y. T., Zelinskiĭ, N. D., Puzitskiĭ, K. V., and Ershov, N. I. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. VII. Effect of Carbon Monoxide Concentration on Its Hydrocondensation With Propylene and *n*-Butylene.] Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1952, pp. 145–151; Chem. Abs., vol. 46, 1952, p. 11,095.

CO concentration was varied 0–22% for propylene and 0–15.8% for *n*–butylene. In both cases hydrocondensation of olefin–H_2 mixtures did not occur in absence of CO and was at maximum for CO content in feed gas of 6–8%. Reactions occurring at low, 6–8%, and high, >approximately 14%, CO content are quite distinct. Rapid decrease of hydrocondensation reaction at CO 15–20% is in contrast to behavior with ethylene, where hydrocondensation still occurs at these concentrations.

Eidus, Y. T., Ershov, N. I., Batuev, M. I., and Zelinskiĭ, N. D. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. VI. Hydrocondensation of Carbon Monoxide With *n*–Butylene.] *See* abs. 802b.

803. Eidus, Y. T., Feditschkina, T. L., Kazanskii, B. A., and Zelinskiĭ, N. D. [Effect of Lowering the Reduction Temperature of the Catalysts Used in the Synthesis of Hydrocarbons from CO and H_2 at Atmospheric Pressure.] Bull. acad. sci. U. R. S. S., classe sci. chim., 1941, pp. 34–40; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 329; Chem. Zentralb., 1942, II, p. 642.

Of the Ni catalysts produced from the oxalate and reduced at 200°, 230°, and 280°, that one reduced at 230° gives the highest contraction. A Ni catalyst obtained from the formate and without previous reduction gave liquid hydrocarbons, but only in small amounts. Ni–Mn–Al_2O_3 catalyst with 6% Cu and 6% Ag is wholly inactive. A Co–Mn catalyst with 10% Cu and without previous reduction gave good results. Catalysts precipitated with soda gave liquid hydrocarbons as well as solid paraffins but deteriorated rapidly.

Eĭdus, Y. T., Zelinskiĭ, N. D., Ershov, N. I., and Batuev, M. I. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. IV. Hydrocondensation of Ethylene With Carbon Monoxide at Low Concentrations of the Latter.] *See* abs. 802.

Eidus, Y. T., Zelinskiĭ, N. D., Puzitskiĭ, K. V., and Ershov, N. I. [Catalytic Hydrocondensation of Carbon Monoxide With Olefins. VII. Effect of Carbon Monoxide Concentration on Its Hydrocondensation With Propylene and *n*–Butylene.] *See* abs. 802c.

804. Eidus, Y. T., Epifanskii, P. F., Petrova, L. V., Elagina, N. V., and Altshuller, S. B. [The Activating Effect of Oxides of Some Metals on the Iron-Copper Contacts Used for Synthesis of Gasoline From Water Gas.] Bull. acad, sci. U. R. S. S., classe sci. chim., 1943, pp. 145–151; U. O. P. Co. Lib. Bull., No. 48, Nov. 29, 1944; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 441; Chem. Abs., vol. 38, 1944, p. 4117.

Investigation of the activating effect of certain metal oxides on the Fe–Cu catalyst under the conditions previously reported in studies of Co and Ni catalysts. The ratio of C to H_2 was 1 : 1. All catalysts tested contained 100 parts Fe, 25 of Cu, 2 of K_2CO_3; and 125 of kieselguhr, plus promoters consisting of oxides of Mn, Mg, Al, and Th used in amount of 2% on the Fe. A catalytic glass tube of 10 mm. diameter containing a layer of catalyst 40 cm. long was used. The experiments were continued from 8–12 hr. at temperatures of 240°–260° in the case of Fe, about 50° lower (180°–210°) with Co or Ni. The latter require a preliminary high-temperature (250°) reduction with H_2 whereas the Fe–Cu catalysts do not. The experimental data show that the activity of the catalyst is affected not only by the method of preparation but by the nature of the metal oxide promoter. The most active catalysts were those precipitated with K and promoted with ThO_2 and MnO. A yield of 79–80 ml. liquid and solid per m.³ initial gas was obtained in presence of a potash-precipitated catalyst promoted with Mn. This was the highest yield obtained. The catalyst promoted with MgO was an exception to the rule in that Na was a more favorable precipitant than K. Another exception was the catalyst promoted with MnO, which was more active when produced by thermal decomposition than by precipitation with Na. Addition of 2 oxides did not raise the activity. The literature reports that Al_2O_3 and ThO_2 inactivate precipitated Fe–Cu catalysts were not confirmed. On the contrary, Al_2O_3 is able to activate Fe–Cu–Mn catalysts if it is added after precipitation of these catalysts. Fe–Cu catalysts are characterized by low stability. The cause may be connected with wax formation. A similar connection was observed for some Co and Ni catalysts.

804a. Eischens, R. P. Exchange Between Chemisorbed and Gaseous Carbon Monoxide on Reduced Iron. Am. Chem. Soc., 120th Meeting Abs., September 1951, p. 15 G.

Exchange between chemisorbed and gaseous CO at —78° goes at markedly different rates on various portions of the Fe surface. There are relatively few of these portions and the rate within each is constant. The exchange goes fastest on the portions where the chemisorption bond is weakest. The most strongly bonded CO is easiest to oxidize to CO_2; however, this observation must be qualified to take into account the

effect of temperature. CO is taken up by "slow chemisorption" or carbonyl formation exchanges at a measurable rate. There is no appreciable difference in the properties of $C^{14}O$ and CO in the chemisorption on Fe.

805. Eisenhut, O., and Kaupp, E. [Radiographic Investigation of the System, Iron–Nitrogen.] Ztschr. Elektrochem., vol. 36, 1930, pp. 392–404; Chem. Abs., vol. 24, 1930, p. 4207.

Phase boundaries, solubility lines, eutectoid lines, and temperatures of Fe–N are definitely fixed by radiograms. The results agree well with data from magnetic analysis. The existence of 4 phases, α, γ, γ' and ϵ is established. There is continuous absorption of N_2 during regular changes of the crystal-lattice constants. Nitrogen martensite is formed. Bibliography included.

806. ———. [Röntgenographic Researches on Iron Catalysts for Ammonia Synthesis.] Ztschr. physik. Chem., vol. 133, 1928. pp. 456–471; Chem. Abs., vol. 22, 1928, p. 3073.

Debye-Scherrer method of powder analysis was used for synthetic NH_3 catalysts, which were prepared according to the patent of the Badische Anilin & Soda-Fabrik (German 249,447, abs. 86), and from complex Fe salts $KAlFe(CN)_6+\chi KCl$. All of these showed principally pure α-Fe, independently of the method of formation or use. The Badische Anilin u. Soda-Fabrik catalyst consisted primarily of Fe_3O_4 in the beginning. The catalyst from the complex salts after reduction also contained Fe_2N, Fe_3C, C, etc. in small quantities.

Eisenstecken, F. *See* abs. 3051.

Elagina, N. V. *See* abs. 790, 796, 804.

Elder, J. L. *See* abs. 740.

807. Eley, D. D. Catalytic Activation of Hydrogen. Advances in Catalysis, Academic Press, Inc., New York, 1948, vol. 1, pp. 157–199.

Report of experimental and theoretical studies on the chemisorption of H_2 on metals. The parahydrogen conversion with reference to the Fischer-Tropsch synthesis is discussed.

808. Eley, D. D., and Rideal, E. K. Catalysis of the Parahydrogen Conversion by Tungsten. Proc. Roy. Soc. (London), vol. 178, A, 1941, pp. 429–451; Chem. Abs., vol. 36, 1942, p. 22.

The p–H_2 conversion was measured on the surface of W as a function of the surface concentration of adsorbed O acting as a poison. The O decreases the fraction of the metal surface available for reaction and affects the reactivity of the neighboring chemisorbed hydrogen. Dipole-dipole interaction between the adsorbed atoms may be an important factor in this. A part of the O adsorbed on W can be removed at room temperature by reaction with H_2. Films of CO, N_2, and C_2H_4 also act as poisons, and it appears that the small conversion that takes place when they are present is due to the formation of a hydride surface on top of the film rather than on gaps in it. Constants for the reaction are calculated, including the temperature-independent factor for the zero order reaction. The reaction is considered in terms of the activated complex theory and is shown to be more in accordance with a conversion mechanism based upon an interchange between loosely adsorbed H_2 molecules and chemisorbed H than with the original idea of the recombination of chemisorbed H_2 atoms. The H_2+D_2 reaction has the same rate as the p–H_2 conversion; hence tunneling in the potential barriers plays an unimportant part in this H_2 reaction, even at —150°. The H_2+D_2 reaction has about the same activation energy as the parahydrogen conversion. This, measured at 1.3 mm., is 3,070 cal. The 2 reactions are kinetically identical and go through the same mechanism.

Elfstrom, N. *See* abs. 1623.

809. Elian, J. [Synthesis of Liquid Hydrocarbons by the Induschimie-Carsyn Process.] Induschimie Fabricators for the Chemical Industries. Brussels, 1941, 23 pp.

Prospectus briefly reviews development of the Fischer-Tropsch process, discusses reaction mechanism based on the carbide theory, and gives an economic study of the process with calculations on the cost of production of primary oil. The conclusions are based largely on the results of experiments carried out over a period of time at the University of Liège. The chief modification resulting from the research is in the use of active metal carbides as catalysts. It is stated that yields have been increased thereby by about 45%, and a more precise control of the nature of the product is obtained. A flow sheet of the process illustrates the synthesis of liquid hydrocarbons from natural gas or byproduct gases from petroleum refining. The process is patented, and the Ruhrchemie A.–G. controls the rights in Germany for utilization of the patent on catalysts. (*See* U. S. Patent 2,369,548.)

810. Eliot, T. Q., Goddin, C. S., and Pace, B. S. Chemicals From Hydrocarbon Synthesis. Oil Gas Jour., vol. 48, No. 1, 1949, p. 112.

Abstract of paper presented at American Institue of Chemical Engineers meeting, Tulsa. Commercial hydrocarbon-synthesis plants in this country, based upon a modified Fischer-Tropsch reaction, will produce a variety of aliphatic oxygenated compounds as byproducts. Typical yields of chemicals are presented for a commercial hydrocarbon plant designed to produce 7,000 bbl. per day of liquid hydrocarbons from natural gas. The distribution of these chemicals, ranging from low-molecular weight, water-soluble materials to high-molecular-weight, oil-soluble materials, is reviewed. Recovery of the byproduct chemicals as crude mixtures from the several synthesis product streams is described. Emphasis is placed upon problems relating to the separation and manufacture of specification-grade chemicals from these crude mixtures. The need for additional fundamental data on physical properties and equilibrium behavior of the individual components and mixtures is indicated.

Elkin, E. M. *See* abs. 3264, 3265, 3266.

Elliott, M. A. *See* abs. 53, 2615.

810a. Elliott, M. A., Perry, H., Johakin, J., Corey, R. C., and Khullar, M. L. Gasification of Pulverized Coal With Oxygen and Steam in a Vortex Reactor. Ind. Eng. Chem., vol. 44, 1952, pp. 1,074–1,082.

An experimental study has been made of the gasification of pulverized bituminous C coal with O_2 and steam in a vortex-type reactor at atmospheric pressure. The potentialities of this type of reactor for producing synthesis gas were investigated. The unit was operated downflow with continuous removal of slag. Most of the data was obtained in coal throughputs of 100 lb. per hr., steam : coal ratio of about 0.5 lb. per lb. of coal, and O_2: coal ratio ranging 7–11 ft.³ per lb. of coal. The O_2 and steam feed streams could be preheated to 1,300° F. All tests were made at a constant reactor diameter of 2 ft. with a 4-in.-diameter outlet, but with reactor depths of 8, 24 and 36 in. In most of the tests, all of the O_2 entered the reactor through tangential slots at the periphery. In some tests, part of the O_2 entered the vortex just beneath the coal stream. The coal was always fed to the reactor from a rotating, H_2O-cooled plate at the top. The effect of ratio of O_2: coal and depth of reactor on C conversion, production of CO+H_2 per lb. of coal and per ft.³ of O_2, are shown and discussed in detail. The best gasification results were obtained when part of the O_2 was admitted with the coal. For example, in the 36-in. vortex the C conversion ranged 78–94% for the range of O_2: coal ratio of 8–11 ft.³ O_2 per lb of coal. At

8 ft.^{3} of O_2 per lb. of coal, approximately 41 lb. of coal and 329 ft.^{3} of O_2 were required for the production of 1,000 ft.^{3} of $CO+H_2$, even with heat losses from the shell of about 1,000 B. t. u. per lb. of coal. This heat loss is thermodynamically equivalent to an O_2 consumption of about 80 ft.^{3} per 1,000 ft.^{3} of $CO+H_2$ The critical factors to be considered in interpreting experimental results on the suspension gasification of coal with O_2 and steam are discussed.

811. Ellis, C. Hydrogenation of Organic Substances. Van Nostrand Co., New York, 1930, 3d ed., chap. LIII–LV, 986 pp.

Reduction of C oxides: MeOH, synthol, and synthine.

812. ———. Lecture Notes on a Visit to Plants of the I. G. Farbenindustrie A.-G. During 1930. Trans. Am. Inst. Chem. Eng., vol. 25, 1930, pp. 16–41; Chem. Abs., vol. 25, 1931, p. 4636.

Illustrated description of the I. G. plants at Oppau and Ludwigshafen with a discussion of the production of synthetic NH_3 and MeOH and the hydrogenation of mineral oils.

813. ———. Chemistry of Petroleum Derivatives. Reinhold Publishing Corp., New York, 1937, vol. II, chap. 52. pp. 1223–1255.

Reduction of CO to hydrocarbons is reviewed, giving 175 refs.

814. Elovich, S. Y., and Zhabrova, G. M. [Mechanism of the Catalytic Hydrogenation of Ethylene on Nickel. I. Kinetics of the Process.] Jour. Phys. Chem. (U. S. S. R.), vol. 13. 1939, pp. 1761–1764; Chem. Abs., vol. 35, 1941, p. 373.

815. ———. [Mechanism of the Catalytic Hydrogenation of Ethylene on Nickel. II. Role of the Activated Adsorption of Ethlyene and Hydrogen in the Hydrogenation Process. General Scheme of the Process.] Jour. Phys. Chem. (U. S. S. R.), vol. 13, 1939, pp. 1775–1786; Chem. Abs., vol. 35, 1941, p. 373.

Within the temperature region in which hydrogenation occurs, both H_2 and C_2H_4 undergo activated adsorption on a Ni catalyst prepared by reduction of NiO. The equation $dq/dt=ae^{-aq}$ holds for all 3 processes. The energy of activation for the activated adsorption for H_2 is 16±1 cal. and for C_2H_4, 9 cal. The initial hydrogenation velocity is 40–60 times as great as the rate of activated adsorption. When the reaction is carried out stepwise, that is, adsorption of H_2 and then of C_2H_4, or the reverse, no hydrogenation takes place. The experimental results can be explained by the following mechanism: $H_2+Ni=H_2Ni$ (molecular adsorption): $C_2H_4+Ni=C_2H_4Ni$ (molecular adsorption); $C_2H_4Ni=C_2H_4Ni^*$ (active state); $C_2H_4Ni^*=C_2H_4Ni$ (activated adsorption); $C_2H_4Ni^*+H_2Ni=C_2H_6+Ni$ (reaction). As the temperature rises, the rate of activated adsorption of C_2H_4 increases, relatively, more rapidly than the rate of hydrogenation, until finally its absolute rate is greater also; poisoning of the surface results, and above a certain temperature of maximum rate of hydrogenation the latter decreases. The temperature for this maximum rate of hydrogenation is lower the more active the catalyst, with respect to activated adsorption and is characteristic for the given catalyst.

816. Elvins, O. C. Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen. Jour. Soc. Chem. Ind., vol. 46, 1927, pp. 473–478T; Chem. Abs., vol. 22, 1928, p. 3130.

Interaction of CO and H_2 was investigated at atmospheric pressure and in presence of catalysts at temperatures of the order of 280°. A catalyst prepared from a mixture of 60 parts of Co, 30 parts of CuO, and 45 parts of MnO was used in conjunction with varying gas mixtures. Contrary to the original statements of Fischer and Tropsch that only aliphatic hydrocarbons are formed by this reaction definite amounts of water-soluble oxygenated compounds and olefins were found among the reaction products. Gives detailed account of the experimental work, and describes preparation of the catalyst from precipitated hydroxides, by ignition of nitrates, and from fused oxides. The size of the granule was also investigated from the point of view of the inherent fouling effect of the waxy products of reaction.

817. Elvins, O. C., and Nash, A. W. Reduction of Carbon Monoxide. Nature, vol. 118, 1926, p. 154; Chem. Abs., vol. 20, 1926, p. 3684.

Formation of hydrocarbons by passing a mixture of CO and H_2 at atmospheric pressure over catalysts has been described by F. Fischer (abs. 1021). Elvins and Nash have confirmed the formation of liquid hydrocarbons and also have shown the possibility of the synthesis of oxygenated compounds. A mixture of 53.9% CO and 44.6% H_2 at atmospheric pressure was passed over reduced oxides of Mn, Co, and Cu impregnated with 0.5% Li_2CO_3, at 302°. 1.2 m.^{3} of gas mixture gave 0.5 gm. of solid and 1.4 gm. of yellow oil insoluble in H_2O and H_2O-soluble acids equivalent to 0.33 gm. KOH. Steam distillation from the K salts of the acids gave 0.5 cc. liquid, boiling at 74°–80°, which gave the CHI_3 reaction in the cold. Fischer's theory of intermediate carbide formation does not explain the formation of oxygenated compounds. The production of oxygenated compounds and hydrocarbons may be regarded as being preceded by the hypothetical formation of MeOH, which gives CH_4 and other substances according to the conditions. The reaction may proceed in stages, or the catalyst may accelerate one or more of the possible reactions of CO and H_2. When a mixture of aldehydes, ketones, acids, and hydrocarbons is obtained, both courses may be followed. Most of the products are probably formed simultaneously rather than consecutively.

818. ———. Synthetic Fuel From Carbon Monoxide and Hydrogen. Fuel, vol. 5, 1926, pp. 263–265; Chem. Abs., vol. 20, 1926, p. 2572.

Review of recent work with preliminary notes on new experiments on the conversion of CO and H_2 to a liquid fuel. The catalyst was prepared by mixing, drying, and reducing a mixture of moist hydrated Co, Cu, and Mn oxides with H_2 at 400°. A mixture of equal volumes of CO and H_2 was washed with aqueous KOH and then H_2SO_4 and passed over the catalyst. The amount of CO_2 increased rapidly with the temperature, reaching 10% at 284°. The gases were cooled and led through active charcoal to a gasometer. An oil accumulated on the water, and the charcoal yielded a liquid composed of saturated hydrocarbons.

819. Elworthy, R. T. Synthetic Methanol. Canadian Chem. and Met., vol. 9, 1925, pp. 139–140; Chem. Abs., vol. 19, 1925, p. 2403.

Résumé of the Badische (abs. 1014, 1015), Patart, and Audibert processes for preparing MeOH from water gas and H_2, with a short bibliography. The first process mentioned employs purified water gas containing 60% H_2, and 30% CO, together with CO_2 and N_2, at 200 atm. pressure, over a catalyst maintained at about 400°. Catalysts are mixtures of metal oxides belonging to different groups in the periodic system, as 90 parts ZnO and 10 parts Cr_2O_3; 85 parts ZnO and 15 parts V oxide, or 90 parts CdO and 10 parts Cr_2O_3. Gases used must be purified carefully, particularly for S and volatile Fe compounds. The Merseberg plant produces about 10–20 tons per day at $0.20 per gal. The Patart process (abs. 2141) uses as catalyst 90% CuO and 10% ZnO at temperatures of 400°–420° and at pressures of 150–250 atm. It gives a product at $0.22–$0.32 per gal. Audibert uses catalysts containing suboxides of V, Mn, W, Pb, and Bi. Emphasizes economic importance of these processes.

Emert, O. *See* abs. 2297.

820. Emmett, P. H. Studies on the Mechanism of Ammonia Synthesis Over Iron Catalysts. Jour. Chem. Education, vol. 7, 1930, pp. 2571–2583; Chem. Abs., vol. 25, 1931, p. 453.

Résumé of all published work on the mechanism of catalytic synthesis of NH_3 and on the effect of promoters on the activity of Fe catalysts.

821. ———. Surface-Area Measurements—a New Tool for Studying Contact Catalysts. Advances in Catalysis, Academic Press, Inc., New York, 1948, vol. I, pp. 65–90.

Critical discussion is presented of new developments in the theory and application of surface area measurements in connection with catalytic work. Its application to the preparation of Fischer-Tropsch catalysts is introduced.

821a. ———. Radioisotopes. Oil Gas Jour., vol. 50, No. 21, 1951, pp. 82, 84, 87, 89, 90, 93.

Uses that have been made of radioactive isotopes in the petroleum industry are discussed under 3 headings: (1) Exploration and production of petroleum, (2) refining and distribution of petroleum products, and (3) chemical research as applied to process development or improvement of petroleum products. Experiments on the application of radioactive tracers to the study of the Fischer-Tropsch mechanism of reaction are described. 47 references.

Emmett, P. H. *See* abs. 42, 376, 377, 386, 387, 388, 389, 390, 669, 1358, 1359, 1470, 2006, 2007, 2008, 2009, 2010, 2717a, 2718.

822. Emmett, P. H., and Brunauer, S. The Poisoning Action of Water Vapor at High Pressure on Iron Synthetic Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 2682–2693; Chem. Abs., vol. 24, 1930, p. 4693.

Poisoning of synthetic NH_3 catalysts by water vapor was studied at 450° at pressures as high as 100 atm. and at various partial pressures of H_2O vapor between 0.08 and 0.64%. The amount of O retained by the catalyst is proportional to $\sqrt{P_{H_2O} : P_{H_2}}$ Very active catalysts are capable of retaining more O than less-active catalysts. The poisoning of both doubly and singly promoted catalysts by water vapor is almost entirely reversible, although a slight permanent injury to the catalyst results. A probable mechanism of NH_3 synthesis consists in the reduction by H_2 of surface Fe_4N formed by the reaction of N_2 with surface Fe atoms having average free energies sufficiently in excess of those of normal Fe atoms.

823. ———. Adsorption of Nitrogen by Iron–Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 56, 1934, pp. 35–41; Chem. Abs., vol. 28, 1934, p. 1243.

Rates of adsorption of N_2 by promoted and by pure Fe catalysts were measured over the temperature range 273°–450°. The energy of activation of the adsorption process is about 16,000 cal. Isotherms at 400° and 450° indicate a heat of adsorption of about 35,000 cal. Isotherms taken at −189° are linear with respect to pressure 100–760 mm.

824. ———. Application of Polanyi's Potential Theory to the van der Waals Adsorption of Gases on Iron–Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 57, 1935, pp. 2732–2733; Chem. Abs., vol. 30, 1936, p. 1291.

Potential-volume curves for the adsorption of N and A on a single promoted Fe synthetic–NH_3 catalyst are given. They seem to represent the isotherms very closely throughout the entire pressure range covered including the region concave to the pressure axis where probably less than a molecule layer of gas exists, the linear portion that has been postulated to represent the building up of a 2d layer of gas on the catalyst surface, and the higher-pressure portion, which is convex to the pressure axis and, which, it is generally believed, represents the condensation of the gas to liquid in the capillaries of the adsorbent. The potential curves exhibit no variation with temperature, the −183° and −195.8° points falling on the same curve.

825. ———. Accumulation of Alkali Promoters on Surfaces of Iron–Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 59, 1937, pp. 310–315; Chem. Abs., vol. 31, 1937, p. 2915.

By comparing the adsorption isotherms for N_2 at −183°, CO at −183°, and CO_2 at −78° on various Fe–synthetic-NH_3 catalysts, evidence was obtained to show that a % or so of K_2O in the catalysts will actually cover more than 50% of the surface of the reduced catalyst. Apparently the chemisorption of CO at −183° occurs principally on surface Fe atoms, whereas the chemisorption of CO_2 at −78° occurs on such surface promoter molecules as contain alkali.

826. ———. Use of Adsorption Isotherms for Measuring the Surface Areas of Catalysts and Other Finely Divided Materials. Trans. Electrochem. Soc., vol. 71, 1937, 12 pp. (preprint); Chem. Abs., vol. 31, 1937, p. 3371.

Describes method for measuring the surface areas of catalysts, and of other finely divided substances, by using low-temperature adsorption isotherms of gases such as N_2, A, CO, O_2, and CO_2. Representative isotherms for 2 promoted Fe–synthetic–NH_3 catalysts, pumice, Ni on pumice, and NiO on pumice are presented. In the case of the Fe catalyst, it is shown that if the beginning of the linear portion of the isotherms is interpreted as the point of completion of a unimolecular layer, surface areas can be calculated that are approximately the same for all gases tried. Furthermore, the surface areas so calculated are large enough to accommodate the observed chemisorption of CO at −183° and the largest irreversible adsorption of H observed at −78°–100°. Only in the case of O at −183° is the volume taken up irreversibly by the catalyst several fold greater than a monomolecular layer. Presumably O reacts chemically with the outer layers of Fe atoms even at −183°. The method has so far been applied with apparent success to the catalysts and catalyst supports mentioned above and in addition to 4 other synthetic NH_3 catalysts. 2 Cu catalysts, glaucosil, 2 soils and 2 soil colloids, samples of dry powdered bacteria, Cr oxide gel, and Cr oxide gel that had been glowed at 400°.

827. ———. Use of Low-Temperature van der Waals Adsorption Isotherms in Determining the Surface Area of Iron–Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 59, 1937, pp. 1553–1564; Chem. Abs., vol. 31, 1937, p. 7322.

Adsorption isotherms of N_2 and A at −195.8°; N_2, A, CO, and O_2 at −183°; CH_4 and NO at −140°; N_2O and CO_2 at −78°; NH_3 at −36°; and *n*-butane at 0° on 6 different Fe synthetic–NH_3 catalysts were determined. These isotherms together with data on the chemisorption of CO on the catalysts at −183° and −78° and for the activated adsorption of H_2 appear to afford a means of measuring the absolute and the relative surface areas of the Fe catalysts. Al_2O_3 promoters appear to concentrate on the surfaces of the Fe catalysts.

828. Emmett, P. H., and Cines, M. Surface-Area Measurements on Metal Spheres and Carbon Blacks. Jour. Phys. and Colloid Chem., vol. 51, 1947, pp. 1329–1341; Chem. Abs., vol. 42, 1948, p. 1104.

Comparison of areas obtained by adsorption isotherms for N_2 at 195° on metal powders with those calculated from photomicrographs yields roughness factors in the range 1.1–1.8. Areas determined by the adsorption isotherms for CS_2 and for C_4H_{10} are 20–50% lower than those obtained by using N_2 as adsorbate. Pelletizing carbon black produces no appreciable changes in its surface area per gm.

829. Emmett, P. H., and Harkness, R. W. Adsorption of Hydrogen by Iron-Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 57, 1935, pp. 1631–1635; Chem. Abs., vol. 30, 1936, p. 369.

Experimental evidence is presented to show that the two types of activated adsorption of H_2 that occur on Fe-synthetic-NH_3 catalysts are, in part at least, adsorptions on the surface of the catalysts rather than any type of solution within the metal. The rate of the lower temperature-activated adsorption (type A) agrees closely with that calculated by assuming that all H_2 molecules are adsorbed that strike the catalyst with the observed energy of activation, 10,400 cal.

830. ———. Catalytic Interconversion of *o-p* Hydrogen Over Iron, Platinum and Nickel Catalysts. Jour. Am. Chem. Soc., vol. 57, 1935, pp. 1624–1631; Chem. Abs., vol. 30, 1936, p. 369.

The *o-p* interconversion of H_2 over Fe-synthetic-NH_3 catalyst was studied as a function of the temperature, pressure, time of contact, and presence of various poisons. Both types of activated adsorption of H_2 on Fe are poisons for the conversion of *o-p*-H_2 at liquid-air temperature. The low-temperature *o-p* conversion over Ni and Pt is also inhibited by the activated adsorption of H_2.

831. Emmett, P. H., and Kummer, J. T. [Physical and Chemical Adsorption Studies on Catalysts.] Jour. chim. phys., vol. 47, 1950, pp. 67–73; Chem. Abs., vol. 44, 1950, p. 6711.

Theory for the multilayer adsorption of gases on solids (abs. 389) still appears to yield reliable values for the surface area of porous and finely divided solids, though according to Halsey (abs. 1340, it is doubtful if the assumptions of the theory are valid. N_2^{28} and N_2^{30} react rapidly to form N_2^{29} over Fe catalysts at 450°–500°, contrary to previous conclusions (abs. 1639). Singly promoted Fe-synthetic-NH_3 catalysts rapidly catalyze the reaction $H_2+D_2=2HD$ at −195°, even though D_2 does not remove H adsorbed at −78° or 100° from the surface at −195°. Adsorption measurements indicate the existence of a new type of activated adsorption on Fe capable of occurring rapidly at −195°. Chemisorption measurements, using normal CO as well as radioactive CO, indicate that Fe-synthetic-NH_3 catalysts behave as though half the surface was homogeneous and half heterogeneous. The measurements were made by covering part of the surface with radioactive CO and the remainder with normal CO at low temperatures and then collecting and analyzing the evolved CO for radioactivity as the temperature was slowly raised.

831a. ———. Mechanism Studies of Fischer-Tropsch Synthesis. Proc. 3d World Petrol. Cong., 1951; Fuel Abs., vol. 11, No. 2, 1852, abs. 1299; Fuel, vol. 31, 1952, p. 370.

Tracer experiments using Fe_2C^{14} lead to the conclusion that most of the hydrocarbon synthesis over Fe and Co catalysts does not occur through formation of metallic carbides as intermediates. Adsorption experiments suggest that the carbides by themselves probably are not good catalysts. The use of radioactive CH_4 is recommended as a sensitive means of ascertaining whether or not this gas can be converted into higher hydrocarbons during synthesis. Results on Fe and Co catalysts showed that in synthesis fewer than 0.1% of the C atoms in the higher hydrocarbons came from CH_4, even though radioactive CH_4 was present in a high concentration (about 50%). Measurements of the free energy of formation of Fe_2C and Fe_3C show that the direct reduction of these carbides by H_2 to form olefins or paraffins by hydrocarbons with more than 6 C atoms is thermodynamically unfavorable. This confirms the tracer experiments in indicating that the carbides of Fe and Co are not intermediates in Fischer-Tropsch synthesis. Use of radioactive O-containing organic molecules is useful for obtaining information relative to the nature of the surface complexes serving as intermediates in the Fischer-Tropsch synthesis. Two such experiments using radioactive EtOH as tracer have shown that either this compound or some surface complex formed from it is capable of acting as an intermediate in the synthesis of higher hydrocarbons. Furthermore, about 90% of the added C atoms that transform the C_2 complex to C_3 hydrocarbon add to the C in the CH_2 rather than to the C of the CH_3 group of the adsorbed alcohol. It seems certain that at least over Fe catalysts, and probably over Co, the higher hydrocarbons are built up by successive adsorption of CO molecules on to the catalyst surface adjacent to some intermediate complex. The CO then attaches itself to the intermediate to form momentarily an O-containing complex which in turn is hydrogenated to remove O and then either escapes from the surface as a hydrocarbon or adds another CO to form a complex containing 1 more C atom. It seems improbable that the synthesis over either Fe or Co results from polymerization of CH_2 groups on the surface or from the reduction of carbides as intermediates.

832. Emmett, P. H., and Love, K. S. Reduction by Hydrogen and Thermal Decomposition of Nitrides Made by the Reaction of Ammonia With Various Promoted and Unpromoted Iron-Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 55, 1933, pp. 4043–4050; Chem. Abs., vol. 28, 1934, p. 29.

Fe_4N prepared from active catalysts decomposes more rapidly than that prepared from rather inactive catalysts. The energy of activation of the decomposition is about 50,000 cal. Gives rates and nature of the reduction and decomposition of the nitrides from the various Fe catalysts.

833. Emmett, P. H., and Shultz, J. F. Equilibrium in the System: Carbon Monoxide–Water–Cobalt Oxide–Hydrogen. Free-Energy Changes for the Reaction $CoO+H_2=Co+H_2O$ and the Reaction $Co+1/2\ O_2=CoO$. Jour. Am. Chem. Soc., vol. 51, 1929, pp. 3249–3262; Chem. Abs., vol. 24, 1930, p. 774.

The object was to determine at several temperatures the equilibrium ratio of $H_2O:H_2$ in the presence of Co. CoO, reduced by H_2 at the temperature desired, was subjected to various mixtures of H_2+H_2O, and the effluent gases were analyzed for H_2 and H_2O. A second catalyst was prepared by reducing Co_3O_4 to CoO. Equilibrium was approached at each temperature from both the H_2 and H_2O sides. A modification of the flow system of Pease and Cook, was used. The ratio $H_2O:H_2$ at 335° was 85±5; at 450°, 67±1; at 515°, 57.0±0.3; and at 570°, 50.5±0.2. ΔF°_{298} for the reaction $CoO+H_2=H_2O+Co$ was calculated as −3,678 calories. ΔH_{298} was calculated as −1,646 calories, as compared with −300 calories calculated from the heats of formation of CoO and H_2O. X-ray photographs indicated that at 500° H_2O did not form Co_3O_4 from CoO. ΔF°_{1373} for the formation of CoO from Co and O_2 was calculated as 32,050 calories, and from this, partial pressure of O_2 in equilibrium with CoO and Co at 1,100° was calculated as 0.5×10^{-7} mm. Transformation of hexagonal to cubic Co takes place at 340°–360°.

834. ———. Equilibria in the Iron–Hydrogen–Oxygen System. Indirect Calculation of the Water-Gas Equilibrium Constant. Jour. Am. Chem. Soc., vol. 52, 1930, p. 4268–4285; Chem. Abs., vol. 25, 1931, p. 453.

The equilibrium constant $K=P_{H_2O}/P_{H_2}$ for the reaction $FeO+H_2=Fe+H_2O$ was determined by a flow method. At 600°, 700°, 800°, 900°, and 1,000°, *K* is, respectively, 0.332, 0.422, 0.499, 0.594, and 0.669. For the reaction $Fe_3O_4+H_2=3FeO+H_2O$, *K* is 1.18 at 700° and 2.37 at 800°. The water-gas constants, calculated by combining these Fe–H–O equilibrium values with those for the Fe–C–O system, agree excellently with constants measured directly by Neumann and Kohler.

835. ———. Equilibrium in the System: Co–CO_2–CoO–CO. Indirect Calculation of the Water-Gas Equilibrium Constant. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 1782–1793; Chem. Abs., vol. 24, 1930, p. 3157.

The value of the equilibrium constant $K_1=CO_2/CO$ for the reaction $CoO+CO=Co+CO_2$ was determined by a flow system at 450°, 515°, and 570° to be 489.6, 245.9, and 148.4, respectively. Combination of these values with the previously determined constant $K_2=H_2O/H_2$ for the reaction (abs. 833) $CoO+H_2=Co+H_2O$ gives indirect values for the water gas constant $K=(CO)(H_2O)/(CO_2)(H_2)$ that agree well with the values determined directly by Neumann and Kohler (abs. 2436).

836. Emmett, P. H., Hendricks, S. B., and Brunauer, S. Dissociation Pressure of Fe_4N. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 1456–1464; Chem. Abs., vol. 24, 1930, p. 2940.

By a flow method, it was determined that at 1 atm. pressure the % NH_3 in a gaseous H_2–NH_3 mixture in equilibrium with an Fe–Fe_4N mixture is 36 at 420°, 30 at 444°, 28.5 at 460°, and 17 at 525°. The dissociation pressures of Fe_4N at these respective temperatures are calculated to be 4,250, 4,300, 5,400, and 5,600 atm.

837. Engelhardt, A. [Recovery and Chemical Utilization of Gaseous Hydrocarbons From Fuel Beneficiation and Motor-Fuel Synthesis.] Internat. Cong. Pure Appl. Chem., 10th Conf., Rome, 1938; Brennstoff-Chem., vol. 19, 1938, pp. 297–304; Chem. Abs., vol. 32, 1938, p. 9444.

Address deals with the sources and relative amounts of gaseous hydrocarbons, methods of their recovery, and possibilities of utilization. Because of the short contact time in the benzine synthesis of Fischer-Tropsch, olefinic hydrocarbons are formed. After recycle over the catalyst, the composition of the synthesis gases in volume % is as follows: CO_2, 29; N_2, 15; H_2, 22; CO, 14.4; CH_4, 16; C_2H_4, 0.6; C_nH_{2n}, 1.5–1.8; C_nH_{2n+2}, 1.7–2.1. Changing the reaction conditions might, naturally, yield a gas of different composition. In general the gaseous hydrocarbons with 2 or more C atoms make up 15–20% of the liquid product; their complete utilization is therefore greatly desired, particularly since they are wholly free from S impurities.

Engelhardt, F. *See* abs. 1947, 1951, 1952, 1953, 1953a, 1955.

838. Engels, W. H. [Production of Hydrogen by the Interaction of Carbon Monoxide and Calcium Hydroxide and Acceleration of the Water-Gas Reaction by Means of Iron.] Jour. Gasbeleucht., vol. 62, 1919, pp. 477–483, 493–500; Chem. Abs., vol. 14, 1920, p. 599.

Engels has investigated the conditions under which the reaction between CO and $Ca(OH)_2$ will best serve for the technical production of H_2. An investigation with the purpose of determining whether the course of the reaction for the production of H_2 is represented by the equation $CO+H_2O\rightarrow H_2+CO_2$ or by the equation $Ca(OH)_2+CO_2\rightleftharpoons CaCO_3+H_2$ is detailed. The results indicate that the course of the reaction is determined principally by the latter equation, a little of the H_2, however, resulting from the reaction represented by the first equation. The reaction is best carried out at about 500°. The use of more steam in the water-gas mixture than that corresponding to the vapor pressure of $Ca(OH)_2$ at the temperature employed is to be avoided. The reaction between Co and CaO is accelerated at least elevenfold by the catalytic action of Fe in consequence of the acceleration of the water-gas reaction by this catalyst. The effect of temperature upon the equilibrium of the water-gas reaction is well represented by the thermo-dynamic relation previously deduced by Haber.

839. Engineering. Fischer-Tropsch Hydrogenation Process. Vol. 146, 1938, p. 517; Chem. Age, vol. 38, 1938, p. 164.

The importance of pilot-plant operation to bring out various difficulties not apparent in laboratory investigation is pointed out. It is important to keep the catalyst at the correct temperature. The various ranges of fuels that may be treated and the different types of products obtained are described in detail, and it is stated that Fischer-Tropsch products have a high H_2 content. The primary products may be used for the synthetic production of lubricants. Recent developments have given greater elasticity to the process with respect to the products obtained.

840. ———. Synthetic Liquid Fuels. Vol. 161, 1946, p. 422.

Summary of progress in the United States in producing liquid fuel synthetically by coal hydrogenation, gas synthesis, shale retorting, and distilling agricultural residues.

841. ———. American Synthetic Liquid Fuel Production. Vol. 165, 1948, p. 398.

Review of United States plans for developing a synthetic fuel industry.

Epifanskii, P. F. *See* abs. 804.

842. Epstein, S. Alloys of Iron and Carbon. I. Constitution. McGraw-Hill Book Co., New York, 1936, 476 pp.

Ercole, R. *See* abs. 2401a, 2706c.

843. Erdely, A., and Nash, A. W. Catalysts Used in the Synthesis of Higher Hydrocarbons From Water Gas. Jour. Soc. Chem. Ind., vol. 47, 1928, No. 32, pp. 219–223T; Chem. Abs., vol. 22, 1928, p. 3818.

A continuation of Elvin's experiments (abs. 816). From the experiments with different unpromoted catalysts at 285°, and with a gas mixture containing equal parts of CO and H_2, a Co–Cu–ZnO catalyst appears to be most suitable. After the initial period, its activity was very constant, causing a contraction of about 50% for several days continuous operation. A Co–Cu–Al_2O_3 catalyst gave nearly as satisfactory a performance, although less oil and more H_2O was formed in its presence. The oil yield was highest with an unpromoted Co–Cu catalyst, although the activity of this catalyst decreased most rapidly. A Co–Cu–CeO_2 catalyst gave the lowest yield of H_2O and a fair yield of oil, but although the initial activity of this catalyst was the greatest, its activity decreased about as rapidly as that of the Co–Cu. Catalysts supported on silica gel were as active as the Co–Cu–Mn catalyst only in 1 instance. In this connection, the importance of the relative proportions of catalyst to support was shown. The optimum temperature for the formation of liquid hydrocarbons was found to be 280°–290° for the Co–Cu–Al_2O_3 catalyst. Above 290° CO_2 and CH_4 are the chief products, and below 230° no reaction was observed. An excess of H_2 in the initial gas mixture increased the H_2O formation, while an excess of CO rapidly decreased the activity of the catalyst. The gas velocity exerts a marked influence on the yield of products. The optimum space velocity for the Co–Cu–ZnO catalyst was about 120 vol. of gas per hr. per unit vol. of catalyst.

844. Erdélyi, S. [Production of Liquid Fuels From Gases.] Magyar Mernök-Epiteszegylet Közlönye, vol. 62, 1928, pp. 73–78; Chem. Abs., vol. 23, 1929, p. 2010.

Summarizing description of the methods of Fischer and the I. G. Farbenindustrie.

845. Erdmann, E. Production of Methane From Carbon Monoxide and Hydrogen. Gas World, vol. 55, 1911, pp. 195–197; Jour. Gasbeleucht., vol. 54, 1911, pp. 737–741; Chem. Trade Jour., vol. 49, 1911, p. 175; Chem. Abs., vol. 5, 1911, pp. 3618, 3726.

Commercial process (the Cedford gas process) is described of converting water gas into CH_4 as follows: $CO+3H_2=CH_4+H_2O$. In practice it is necessary to use 5 vol. H_2 : 1 CO. A water gas containing 40% CO, 4% CO_2, 52% H_2, and 4% N_2 after going through the process, contained traces of CO and CO_2, 30% CH_4, 62% H_2 and 6–7% N_2. The total cost was 8.5 d. per 1,000 cu. ft.

845a. Erdöl u. Kohle. Patent Report. Vol. 5, 1952, pp. 585–589; Chem. Abs., vol 47, 1953, p. 290.

List of German and foreign patents on the general subject of coal and oil production and manufacture.

846. Eremenko, V. Y., and Miroshnichenko, G. K. [Thermoanthracite and the Chemical Industry.] Coke and Chem. (U. S. S. R.), No. 2, 1939, pp. 41–46; Khim. Referat. Zhur., No. 8, 1939, pp. 90–91; Chem. Abs., vol. 34, 1940, p. 5625.

During the production of thermoanthracite in the Miroshnichenko furnaces up to 20% of the anthracite is gasified. By blowing with steam–O_2 or air–steam–O_2, the contents of CO and H_2 can be increased to yield a gas suitable for the synthesis of NH_3 or of MeOH. Combined production of thermoanthracite and gas for the synthesis lowers the cost.

Eriksen, A. *See* abs. 2782.

847. Erkko, E. O. [Liquid Fuels.] Suomen Kemistilehti, vol. 8A, 1935, pp. 103–108; Chem. Zentralb., vol. I, 1936, p. 1152; Chem. Abs., vol. 30, 1936, p. 265.

Survey of synthetic methods for the production of liquid fuels.

848. Ernst, F. A. Equipment for High-Pressure Reactions. Ind. Eng. Chem., vol. 18, 1926, pp. 664–669; Chem. and Met. Eng., vol. 33, 1926, pp. 413–414; Chem. Abs., vol. 20, 1926, p. 2765.

Sketches and brief description of various pieces of high-pressure (100–1,000 atm.) equipment for research or experimental work. The apparatus described has been operated satisfactorily at the Fixed Nitrogen Research Laboratory, Washington, D. C. The equipment described includes materials, hydraulic pump, deadweight gage, converter head, electrical connection, tubing and connectors, gas-circulating pump, magnetic pressure-regulating valve, and high-pressure relief valve.

———. *See* abs. 928.

Erofeev, B. V. *See* abs. 1806.

849. Erofeev, B. V., Runtso, A. P., and Volkova, A. A. [Kinetics of the Catalytic Reduction to Hydrocarbons of Carbon Monoxide by Hydrogen on a Cobalt-Thorium Catalyst.] Acta Physicochim. U. R. S. S., vol. 13, 1940, pp. 111–122 (in German); Chem. Abs., vol. 35, 1941, pp. 1690–1691.

Kinetics of the reaction $n\mathrm{CO} + 2n\mathrm{H_2} = \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O}$ at 200° were studied on a Co : Th : SiO_2 = 100 : 15 : 100 catalyst prepared by treatment of the nitrates with K_2CO_3, addition of ethyl orthosilicate, and reduction with H_2 at 400°. With carefully purified H_2 and CO the yield of liquid C_nH_{2n} was 60–70 cc. per m.³ gas. The experimental data satisfy the equations, $A = a + (b/u_0)$, $u_k = cu_0 - b$, $\pi = Au_0 = au_0 + b$, where u_0 and u_k = volume velocity of gas entering and leaving, A = contraction, π = capacity and a, b, c are constants. These results indicate that the reaction is of zero order on a catalytic surface of the first kind. The capacity increases with increasing streaming velocity; this fact indicates that the adsorption of the reaction products depends strongly on their partial pressures; greater streaming velocity increases the surface available for reaction.

Ershov, N. I. *See* abs. 798, 802, 802b, 802c.

850. Eskreis, A. [Conversion of Carbon Monoxide: $CO+H_2O=CO_2+H_2$.] Plyn, Voda zdravotni Technika, vol. 17, 1937, p. 176; Chem. Zentralb., vol. II, 1937, pp. 1486–1487; Chem. Abs., vol. 33, 1939, p. 4763.

For this reaction there is a definite proportion of water vapor that gives the optimum yield. The introduction of superheated steam increases the amount of water vapor and thus improves the effect. The temperature must be maintained within narrow limits. The conversion is retarded not only by the reaction products but also by an excess of one of the reacting substances, that is, the water vapor. The optimum concentration of steam at a given temperature can be calculated from the relation: $(100-q : 100)\eta W'=Q_p-Q_r+Y(\eta A-B)+(B-B')X$. Here q=the percentage heat loss in the reaction space; η=the thermal capacity of the apparatus; W'=the theoretical heat effect of the reaction; Q_p=heat of the products after the reaction at the final temperature of the process; Q_r=the heat of the reactants before the reaction at the initial temperature of the reaction; Y=the theoretical percentage completion of the reaction; B=the molecular specific heat of water at the final temperature; B'=the molecular specific heat of water at the temperature of steam entering the furnace; X=the molecules of water vapor to be added; and A=the molecular specific heat of CO_2 at the final temperature.

851. Estival, J. Gasification of Low-Grade Fuels for the Synthesis of Gasoline and Methanol. Coal Carbonisation, vol. 2, 1936, p. 222; Génie civil, vol. 109, 1937, pp. 405–407; Chem. Abs., vol. 31, 1937, p. 8884.

Philipon gas producer and the installation at Saint Etienne are described. Tests were made in a small gas producer, treating 100–150 kg. per hr., on a lignite from the collieries of Bouches-du-Rhone. A slag suitable for cement manufacture, an iron containing less than 0.10% S, a gas particularly rich in CO and H_2, and some tar were obtained. Results indicate that any fuel, crude, carbonized, or semicarbonized, can be used to produce a gas suitable for the manufacture of MeOH or gasoline. Adaptation to large-scale production and means of reducing costs are discussed. Suggestions for using the gas to make gasoline or MeOH and a drawing of equipment for the manufacture of MeOH are given.

Eth, —. *See* abs. 3728.

852. Eucken, A. [Contact Catalysis.] Naturwissenschaften, vol. 36, 1949, pp. 48–53, 74–81; Chem. Abs., vol. 44, 1950, p. 3777.

Review dealing with general principles, dehydration and dehydrogenation of alcohols on metal oxides, and hydrogenation of unsaturated hydrocarbons on metals; many curves and tabulated data.

852a. ———. [Hydrogenation of Unsaturated Hydrocarbons on Nickel Contact Catalysts. I. Adsorption of Hydrogen on Nickel.] Ztschr. Elektrochem., vol. 53, 1949, pp. 285–290; British Abs., 1951, I, A, p. 52.

Adsorption of H_2 on Ni powder is investigated at constant temperature and also at constant pressure. The

differential or intermediate heat of adsorption is determined calorimetrically. The results agree with the assumption that H_2 is dissociated and is adsorbed in the atomic state. The adsorption velocity is determined. There are 2 maxima in the adsorption velocity isobars, 1 at about 200° abs. and the other at about 270° abs. At higher pressures the 1st maximum disappears. This is not due to the presence of 2 regions of the surface with different activities. It is more likely that changes take place in the whole surface on heating, and that the activity therefore alters. The heat of adsorption decreases relatively strongly with increasing cover density.

853. Eucken, A., and Hunsmann, W. [Calorimetric Study of Physical and Activated Adsorption of Hydrogen on Nickel.] Ztschr. physik. Chem., vol. B 44, 1939, pp. 163–184; Chem. Abs., vol. 34, 1940, p. 666.

Heat of adsorption of H_2 on Ni was studied calorimetrically, 20°–273° K. Desorption was also measured in the same temperature range with a hot-wire manometer. 2 heats of activation for desorption were detected: 1 corresponds to 14% of the adsorbing centers and amounts to 9–10 kcal. per mol; the other accounts for the remaining 86% and is 18–22 kcal. per mol. The heat of adsorption increases linearly from 4–21 kg.-cal. per mol. The van der Waals heat of adsorption is about 800 cal. per mol. and depends strongly on the density of coverage of the surface. Low-temperature tunnel effects could not be detected.

Evans, G. M. *See* abs. 3657.

854. Evans, H. P., and Hayes, A. Graphitizing Behavior of Iron Carbide in Pure Iron–Carbon Alloys in the Critical-Range. Trans. Am. Soc. Steel Treating, vol. 11, 1927, pp. 691–707; Chem. Abs., vol. 21, 1927, p. 3878.

Fe–C alloys of high purity have been graphitized in the presence of a CO–CO_2 gas mixture at a pressure of 5 atm. within the temperature interval 1,292°–1,875° F. Fe_3C in Fe–C alloys of high purity and containing about 2.3% C is metastable at temperatures below 1,292° F. and above 1,562° F. in the presence of this CO–CO_2 gas mixture when it is applied at a pressure of 5 atm.

Evans, R. M. *See* abs. 763.

855. Evans, R. M., and Newton, W. L. Hydrogen From Water Gas. Ind. Eng. Chem., vol. 18, 1926, pp. 513–517; Chem. Abs., vol. 20, 1926, p. 2242.

Catalysts for the Bosch or "catalytic water gas" process for H_2 production by interacting the CO of the water gas with steam (and later removing the CO_2 thus formed) have been studied in detail. With an oxide catalyst containing 97% Co, 2% Al, and 1% K and a space velocity per hr. of 1,000 at 450° and at 350°, the % CO in the dry effluent gas was reduced to 1.1 and 0.3, respectively, these corresponding to the equilibrium values. Substitution of the Co, partly or wholly, by Fe produced only slightly less efficient catalysts. The Co catalysts are slowly poisoned even by small quantities of H_2S, CS_2, or COS, so that careful purification would be necessary in operation, but the Fe catalysts are less sensitive and probably could function continuously on unpurified water gas from a good grade of coke.

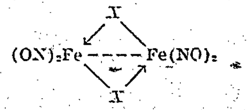
Eventova, M. S. *See* abs. 306.

856. Ewell, R. H. Calculation of Chemical Equilibrium at High Pressures. Ind. Eng. Chem., vol. 32, 1940, pp. 147–153; Chem. Abs., vol. 34, 1940, p. 3158.

Starting with the 3d law of thermodynamics, the general expression for equilibrium constants is derived and applied to the synthesis of MeOH from CO and steam. Fugacities and activity coefficients are reviewed, and Berthelot's equation of state and a new modification of the van der Waals equation are brought out. The use of Raoult's law in calculating high-pressure equilibrium in the manufacture of MeOH is indicated.

857. Ewens, R. V. G. Constitution of Certain Binuclear Metallic Carbonyls and Nitrosyls. Nature, vol. 161, 1948, pp. 530–531; Chem. Abs., vol. 42, 1948, p. 4484.

Discussion of the resonance structure proposed by Jensen and Asmussen for $Fe_2(CO)_9$. A covalent Fe–Fe link is preferred on the basis of X-ray and diamagnetic data, as well as color (*see* Powell and Ewens, abs. 2736). Structures of a similar nature are proposed for $Co_2(CO)_8$, Fe nitrosyl compounds, $Fe(NO)_2X$, where X is SK, Cl, I, SC_2H_5, SC_6H_5, or S_2O_3K.



———. *See* abs. 2736.

Ewig, K. *See* abs. 3324.

858. Eyber, G. [Photochemical Decomposition of Iron Pentacarbonyl.] Ztschr. physik. Chem., vol. 144 A, 1929, pp. 1–21; Chem. Abs., vol. 24, 1930, p. 553.

Eyber has investigated the absorption spectrum of hexane solutions of $Fe(CO)_5$ and finds strong absorption below about 4,600 Å. U. The decomposition of the vapor by radiation of wave length, 4,000 Å. U., has been studied. A quantum efficiency of 2 is found. This is explained by the postulation of the formation of an activated molecule that reacts with a normal molecule to give CO and $Fe_2(CO)_9$. Foreign gases (CO_2, A, N_2 and CO) inhibit the decomposition; a deactivation of the excited molecule may be the reason.

$$d(\mathrm{CO})/dt=\frac{K_1(I_{\mathrm{abs.}})}{1+(K_3/K_2)\cdot[(G)/(C)]}$$

where (G) is foreign gas and (C) is pentacarbonyl, satisfies the data. O_2, if present, alters the reaction. The vapor-pressure curve from −14° to +20° has been determined.

859. Eyraud, I. [Automatic Adsorption Balance.] Jour. chim. phys., vol. 47, 1950, pp. 104–107; Chem. Abs., vol. 44, 1950, p. 7095.

Details of construction for a sensitive adsorption balance capable of automatically recording and plotting a curve for the rate of adsorption of a gas by a solid.

F

860. Faber, A. [Natural and Artificial Mineral Oils in Germany, 1914–17.] Petrol. Ztschr., vol. 24, 1928, pp. 644–652; Chem. Abs., vol. 23, 1929, p. 267.

German oil production, consumption, and import statistics. A general discussion of the possible future supply from coal points to the most economical production by coal distillation to produce tar oil and coke, the coke being gasified with steam to produce water gas, which may be used in the production of synthetic motor fuel. The coal tar serves as a basis for diesel and fuel oils.

861. Fabre, R. [Synthetic Methanol.] Jour. pharm. chim. (8), vol. 2, 1925, pp. 113–117; Chem. Abs., vol. 20, 1926, p. 1216.

Review.

Fairfield, R. G. *See* abs. 202, 1708.

Fairlie, D. M. *See* abs. 2749, 2750, 2751.

862. Falcke, V. [Reaction Between Ferrous Oxide and Carbon and Between Carbon Monoxide and Iron. I.] Ber. deut. chem. Gesell., vol. 46, 1913, pp. 743–750; Jour. Soc. Chem. Ind., vol. 32, 1913, p. 365; Chem. Abs., vol. 7, 1913, p. 2525.

The above reaction was studied to ascertain whether or not any difference could be detected between the various kinds of amorphous C, the method being to determine the equilibrium pressure. Experiments showed that FeO prepared by heating FeC_2O_4 at 300° is not pure, and that gas is still given off after the solid has been heated to 700°. Addition of amorphous C has no effect on the pressure produced when FeO, containing 0.5% C, and Fe are heated together at 530°–660°; further, the reaction between FeO and CO is different when the CO is passed over the FeO and when the 2 are heated together in a closed vessel, in the 1st. case much C being deposited, in the 2d, none. When the product obtained in the latter case is dissolved in HCl, no C is deposited, but much CO_2 is evolved.

863. ———. [Reaction Between Ferrous Oxide and Carbon and Between Carbon Monoxide and Iron. II.] Ztschr. Elektrochem., vol. 21, 1915, pp. 37–50; Jour. Soc. Chem. Ind., vol. 34, 1915, p. 554; Chem. Abs., vol. 9, 1915, p. 1883.

The author has studied these reactions at temperatures ranging from 600° upward, and has examined the gaseous products obtained when the reaction mixtures were dissolved in HCl. 3 varieties of graphite and 5 of amorphous C were used. After thorough purification these were analyzed and their densities determined. The apparatus was one used in previous work (abs. 862). The solid mixtures were introduced in the form of compressed pellets. Below 650° the highly purified varieties of C do not react with FeO, and above this temperature the several varieties of C do not behave alike and may be classed in 3 groups. Sugar charcoal and that obtained by the action of CO on Na are quite inactive up to 800°. C obtained by burning C_2H_2 in Cl and that from petroleum reacted with vigor at 650°. It is not known whether the different in behavior is a property of the different modifications or the result of catalytic action. The graphites reacted vigorously also. The products of the reaction of C and FeO contained pure Fe, and no hydrocarbons resulted from solution in HCl. When Fe was permitted to absorb a large quantity of CO and the equilibrium pressure set up at 600°, the product of the reaction that took place yielded large amounts of saturated hydrocarbons, chiefly C_2H_6, when treated with HCl. No solid C remained. On the contrary, when Fe was heated in a stream of CO or allowed to absorb CO in large amounts, and then heated in a vacuum, the product treated with HCl gave no hydrocarbons and a residue of C resulted.

864. ———. [Reactions Between Ferrous Oxide and Carbon and Between Carbon Monoxide and Iron. III.] Ztsch. Elektrochem., vol. 22, 1916, pp. 121–133; Jour. Chem. Soc., vol. 110, II, p. 484; Chem. Abs., vol. 10, 1916, p. 3041.

Continuation of experiments already described (abs. 863). Experiments are made to compare the author's values directly with those of Schenck (abs. 3064, 3073).

865. ———. [Reactions Between Ferrous Oxide and Carbon and Between Carbon Monoxide and Iron. IV.] Ztschr. Elektrochem., vol. 27, 1921, pp. 268–278; Chem. Abs., vol. 15, 1921, p. 3017.

Previous investigations on the equilibrium of the reactions between FeO and C and between CO and Fe are discussed briefly. It has been found experimentally that at temperatures under 700° the equilibrium constant,

$$\xi=\frac{p^2CO}{pCO_2\cdot RT\cdot 760}$$

of the reaction $C+CO_2\rightleftharpoons 2CO$, does not coincide with that obtained from measurements of the equilibrium of the reaction between FeO and C and between CO and Fe. From both this and analytical data it would appear that in this equilibrium the C does not play a role as a definite phase. The most probable explanation of this phenomenon is the previously accepted surmise that the equilibrium is determined by the formation of carbide.

866. ———. [Equilibrium $C+CO_2\rightleftharpoons 2CO$. Thermodynamics of the Blast-Furnace Process.] Ztschr. Elektrochem., vol. 33, 1927, pp. 1–11; British Chem. Abs., 1927, B, p. 191.

Values recorded in the literature for the equilibrium constant, $k=[CO]^2/[CO_2]$, at various temperatures (523°–1,150°) have been collected and compared by plotting on a log k–T diagram: Corresponding values for the heat of reaction, q, have been calculated from those of k. Independent sets of values for k and q have been calculated from specific heat data and figures for the heats of combustion of C and CO. At a given temperature 2 values of k (calculated), and similarly of q (calculated), are obtained according to whether graphite or amorphous C is regarded as participating in the reaction; but for k (calculated) the difference becomes inappreciable at the higher temperatures. Above 750° values of k (experimental) agree well among themselves and with the corresponding calculated values, but at lower temperatures they are somewhat irregular. Comparison of values of q (from experimental k) with those of q (calculated) shows that above about 750° the former fit in with the assumption that graphite participates in the equilibrium, whereas, at lower temperatures they correspond more closely to values for amorphous C. Values of k (experimental) obtained from equilibria reached from the CO side in the presence of Fe powder diverge notably from those obtained in other ways when the equilibrium temperature is below 750°. This discrepancy is ascribed to the abnormal condition of the C in the iron; it is markedly reduced if the Fe is previously treated with CO for a long time so that free C may be deposited in it. In any case, the establishment of equilibrium is undoubtedly slow at the lower temperatures, and is not well-defined. Measurements of k derived from the composition of blast-furnace gases have also been collected on log k–T diagrams. They are very irregular at lower temperatures, but correspond approximately with the experimental and calculated values at temperatures above about 750°. Thus the equilibrium $C+CO_2\rightleftharpoons 2CO$ is only attained in the blast furnace gases at these higher temperatures.

867. ———. [Reactions Between Ferrous Oxide and Carbon and Between Carbon Monoxide and Iron.] Ztschr. Elektrochem., vol. 34, 1928, pp. 393–398; Chem. Abs., vol. 23, 1929, p. 2086.

Polemical. Criticism of the work of R. Schenck (abs. 3049).

———. *See* abs. 3073.

868. Falcke, V., and Fischer, W. [Equilibrium Between Carbon Monoxide, Carbon and Carbon Dioxide. Reaction Between Ferrous Oxide and Carbon, and Between Carbon Monoxide and Iron.] Ztschr. Elektrochem., vol. 32, 1926, pp. 194–201; Chem. Abs., vol. 20, 1926, p. 3626.

Numerous determinations of the equilibrium constant for the reaction $C+CO_2=2CO$ may be expressed log $K_p=-(8351/T)+0.242\ \log\ T-5.65\times 10^{-4}T+4.60\times 10^{-8}T^2-\log\ T+9.504$. The heat of the reaction (van't Hoff equation) is 36,600 cal. at $T=958$. In the presence of excess free Fe the reaction is not $CO_2+Fe=CO+FeO$. Fe_3C is formed and hence in presence of Fe, not saturated with C, the equilibrium constants deviate from the above equation decidedly.

Fallot, M. *See* abs. 1279.

869. Falmouth, Viscount (Chairman). Falmouth Report on Oil From Coal. Rept. of Comm. of Imperial Defense, Subcomm. on Oil from Coal. H. M. S. Office, London, 1938, 71 pp; Engineering, vol. 145, 1938, pp. 211–212; Engineer, vol. 165, 1938, pp. 215–216, 223, 241–243; Chem. Age, vol. 38, 1938, pp. 141–143; Colliery Guard., vol. 156, 1938, pp. 307–309, 346–347; Iron and Coal Trades Rev., vol. 136, 1938, pp. 326, 356.

870. Faltin, H. [Problems of Heat Transmission in the Construction of Contact Synthesis Furnaces.] Die Technik, vol. 3, 1948, pp. 457–464; Chem. Abs., vol. 43, 1949, p. 2475.

Effect of the heats of reaction in both endothermal and exothermal processes on the requirements of available space in the reaction chamber and arrangements for carrying away the heat developed or supplying any heat required to make the process isothermal are discussed. Furnace design is explained. Endothermal processes comprise disintegration of CO_2 into CO and O, or dehydration. Exothermal processes are oxidation, hydration, chlorination, polymerization, etc.

Fankuchen, I. *See* abs. 1617.

871. Fanning, L. M. Gasoline Substitutes Gain in Europe. Oil Gas Jour., vol. 34, No. 34, 1926, pp. 142, 150; Chem. Abs., vol. 20, 1926, p. 1706.

General discussion of the synthetic fuel situation.

Fano, U. *See* abs. 3027.

Faragher, W. F. *See* abs. 1494, 1495, 3393.

872. Faragher, W. F. and Horne, W. A. Interrogation of Dr. H. Pichler and Professor Ziegler at Kaiser Wilhelm Institut für Kohlenforschung, Mülheim. FIAT Rept. 276; PB 1,058, 1291.

Gives further information on isosynthesis and the results of comparative tests on Fe Fischer-Tropsch catalysts conducted at Schwarzheide-Ruhland. Supplements information previously given in abs. 1302.

873. Faragher, W. F., Horne, W. A., Howes, D. A., Schindler, H., Chaffee, C. C., West, H. L., and Rosenfeld, L. Supplemental Report on Ruhrchemie A.-G., Sterkrade-Holten, Ruhr. CIOS Report XXXII–96, 1945, 92 pp. TOM Reel 196; PB 1366; British Abs., 1948, B II, p. 287.

Contains information on the manufacture of toluene from n-heptane, synthetic lubricating oil from Fischer-Tropsch olefins, a laboratory test for activity of the Fischer Co catalyst, an estimate of the operating costs of the Oxo process, the direct synthesis of higher alcohols from water gas, preparation of the Fe Fischer catalyst, the methanization of coke-oven gas-catalyst and process, oxidation of paraffin wax with N oxides to produce fatty acids, product testing and utilization of fuels and lubricating oils produced by Ruhrchemie A.-G.

874. ———. Supplemental Report on Ruhrchemie A. G., Sterkrade-Holten, Ruhr. Synthetic Lubricating Oil Manufacture. CIOS Rept. XXXII–96, 1945, pp. 5–13; TOM Reel 196; PB 1366.

Raw material for the manufacture of synthetic lubricating oil by the Ruhrchemie process consists of olefins in the gasoline boiling range having 1 double bond at the end of the chain that are obtained by cracking Fischer-Tropsch gas oil and sweet oil from Fischer-Tropsch wax. Gas oil from plants operating at atmospheric pressure or at 10–15 atm. is suitable. The gas oil has a boiling range of about 230°–320°. The feed stock, thus obtained, and containing not more than 0.015% of H_2O, is polymerized in the presence of 1.2–1.5% of $AlCl_3$, the temperature being gradually raised from 40° to 100° over a period of 4–6 hr. The synthetic oil product is separated from the catalyst-complex oil by settling; dechlorinated by treatment with 1.5% each of Tonsil, HCl activated clay, and ZnO at 180° for 3 hr.; and double distilled, yielding about 33% gasoline, naphtha diesel oil and spindle oil and 64% lubricating oil, 3% being lost. The finished motor oil has a density at 20° of 0.855, viscosity at 50° 7E° and pole height 1.75. Owing to the unsaturated character of the synthetic oil, it was very unstable toward oxidation and only a temporary improvement was obtained by subjecting it to a second treatment with 1% $AlCl_3$ at 180° for 3 hr. A more permanent improvement was obtained by adding 0.2–0.5% by weight of phenthiazin to the olefins before polymerization. Another method was to add 0.3–0.5% by weight of S to the feed stock before polymerization and then treating the oil with 1% by weight of $AlCl_3$ at 250° for 5 hr. The viscosity of the finished oil could be changed by changing the conditions of polymerization. Using 1.5% by weight of $AlCl_3$ and keeping the temperature at 100° from the start of the reaction gave an oil of low viscosity, 4° E at 50°, whereas when 4–6% $AlCl_3$ is used and the temperature kept at 15° for 12–20 hr. followed by heating to 60° for 2 hr., an oil of 38° E at 50° is obtained. The viscosity index and resistance to oxidation were also improved by using olefins with longer chains. In making aviation grade bright stock by the so-called Synthol process, a different feed stock had to be used; only olefins from C_9 to C_{15} were to be used and these supplemented with C_6 to C_{10} olefins obtained directly by the Recycle process and by the C_{15} to C_{18} paraffins, which remain unreacted in the Oxo process. The Recycle process, designed for the manufacture of olefins, consists in using 1 vol. of water gas containing 87% of CO and H_2 ($CO : H_2 = 1 : 1.23$–1.25) with 3 vol. of recycle gas from the synthesis so that the $CO : H_2 = 1 : 0.8$. The catalyst is 100 Co, 15 MgO, 200 kieselguhr, the temp. of the synthesis 200°–220°, pressure 10–15 atm., the space velocity 800 m.^{3} gas per 10 m.^{3} catalyst per hr. The total yield of liquid products and gasol amounts to 160 gm. per m.^{3} of ideal gas. The polymerization procedure varied somewhat from that followed in the manufacture of motor lubricant; it was planned to use 4–6% by weight of $AlCl_3$, react the olefins for 10 hr. with the catalyst at 15° and then heat for 2 hr. at 60°. Phentiazen was to be added to the olefins before polymerization. A flowsheet shows the complete process.

875. ———. Supplemental Report on Ruhrchemie, A. G., Sterkrade-Holten, Ruhr. Laboratory Test for Activity of Fischer Catalyst. CIOS Rept. XXXII–96, 1945, pp. 14–16; TOM Reel 196; PB 1366.

About 4 gm. of catalyst in a glass tube are reduced for 2 hr. at 450° with a mixture of H_2 and N_2 (3 : 1) at the rate of 300 l. per hr. or with pure H_2 at 400°. The final catalyst contains 40–50% of the Co as oxide. After reduction, the tube is placed in an Al-block furnace and treated with synthesis gas (4 l. $CO:H_2=1.0:1.8$–1.9) for 500 hr. Contraction of the gas volume and yield of liquid products are measured and serve as measures of activity. The liquid products are expressed as cc. per N m.^{3} of synthesis gas and comprise oil that condenses at room temperature in the receiver and the liquid removed from the activated C adsorber by steaming at 150° and 15–20 mm. Hg. Water formation can also be used in appraising the catalyst activity. A diagram of the apparatus is shown, and typical test data for a normal Co catalyst and its contraction curve are attached.

876. ———. Supplemental Report on Ruhrchemie A.-G., Sterkrade-Holten, Ruhr. Oxo Process. CIOS Rept. XXXII–96, 1945, pp. 17–19; TOM Reel 196; PB 1366.

Economic estimate as of Mar. 4, 1943, is given of the operating costs for 12,000 tons per yr. of fatty alcohols based on pilot-plant operation, 1/10 commercial size. Material input was 12,000 tons olefins at RM 0.40 per kgm., 6,000,000 N m.^{3} water gas at RM 0.04 per N m.^{3}, 3,000,000 N m.^{3} H_2 at RM 0.075 per N m.^{3} with total material, operating and capital costs of RM 9,387,070 or RM 78.23 per 100 kg. fatty alcohol. 2 flow sheets of the process are attached.

877. ———. Supplemental Report on Ruhrchemie A.-G., Sterkrade-Holten, Ruhr. Direct Synthesis of Higher Alcohols From Water Gas. CIOS Rept. XXXII-96, 1945, pp. 20–21; TOM Reel 196; PB 1366.

Direct synthesis of alcohols was being studied in the small unit show schematically. The process involves passing a mixture of fresh water gas and recycle gas compressed in 2 stages to 10–100 atm. at a space velocity of 100–150 N l. per l. of catalyst per hr. over 5 l. of a promoted Fe catalyst (100 Fe, 5 Cu, 10 Ce, 50 kieselguhr) contained in an oil-heated tubular reactor. The reaction products are passed through a hot separator at 110° and thence to a condenser. The gas flow is started at a reactor temperature of 200°, which is raised degree by degree to the desired conversion temperature, 220°–240°. At the higher pressure the olefin content of the product is small and the O-containing products are of shorter chain length, whereas at medium pressure higher molecular compounds are formed with a higher proportion of olefins. From 1 N m.^{3} of gas, 80–100 gm. of a mixture of alcohols, esters, and olefins, to about C_{18}, are obtained in a single pass operation. The alcohol content of the total product averages 50–60% and the alcohols are all primary and predominantly of iso-structure.

878. ———. Supplemental Report on Ruhrchemie A.-G., Sterkrade-Holten, Ruhr. The Ruhrchemie Iron Fischer Catalyst. CIOS Rept. XXXII-96, 1945, pp. 22–26; TOM Reel 196; PB 1366.

Preparation of a new Fe catalyst to replace the previously used dense sintered Fe catalyst is described. The new catalyst is made by dissolving the components, Cu, Fe, and CaO in that order in a 50% concentration of technical HNO_3, heating the solution to boiling for several hours and then cooling it to room temperature. Thus prepared, the solution contains little free HNO_3, is stable and does not form a deposit; the content of the components is within the following ranges: Fe, 115–125; Cu, 5–7; and CaO, 11–13 gm. per l. Total HNO_3 is 510–450 gm. Before precipitation, the concentration of the Fe is brought to 50–55 gm. per 1. Precipitation from the mixed nitrates is accomplished by introducing the solution heated to 98° into a boiling solution of Na_2CO_3 of a concentration of 90–100 gm. per l. while stirring intensively. The amount of Na_2CO_3 used is such that, at the end of the precipitation, the *p*H is 6.8. Total time of precipitation must not exceed 5 min. After evolution of CO_2 is ended, the calculated amount of kieselguhr is stirred into the mixture, the suspension is filtered and washed with hot condensate down to 0.4–0.6% of $NaNO_3$, the cake is impregnated with 3.0–3.5% of KOH based on the Fe, the filter is pressed again, and then is dried at 110°. The catalyst thus prepared is hard and resistant to abrasion. The finished catalyst has the following proportions: 100 Fe; 5 Cu; 8 CaO; 30 kieselguhr. Reduction of the catalyst takes place with a mixture of H_2 and N_2 (3 : 1) for 30 min. at a maximum temperature of 300°. When H_2 only is used the time is much shorter. The rate of gas flow is about 2,000 m.^{3} per hr. per m.^{2} of cross section. A content of more than 5–8% of metallic Fe in the finished reduced catalyst must be avoided as higher contents give an inactive catalyst. Furthermore, the Fe soluble in 2% solution of acetic acid shall be 60–70% of the total Fe. After reduction the catalyst is treated in the usual manner with cold N_2 and then saturated with CO_2. The saturation must be conducted slowly since considerable heat is liberated.

Farcas, T. *See* abs. 2755.

879. Farish, W. S. Manufacture of Gasoline and Oil From Coal. Synthetic Liquid Fuels Hearings Before a Subcommittee of the Committee on Public Lands and Surveys, U. S. Senate, 78th Cong., 1st Sess., on S. 1243, 1944, pp. 51–59.

Survey of the economics of the Bergius coal hydrogenation and the Fischer-Tropsch synthesis processes for the production of gasoline. The paper summarizes the raw material and overall steel requirements, as well as investments and operating costs. Figures are on the basis of 1942 estimate.

Cost estimates on synthetic liquid fuel processes if operated in the United States in 1942

	Approx. plant investment per bbl. gasoline per day	Approx. tons steel per bbl. gasoline per day	Approx. cost of gasoline per gal. without depreciation	Approx. gasoline total cost, including depreciation
1. High-pressure coal hydrogenation	$12,800.00	14.1	$0.159	$0.226
2. Fischer process, Europe design, from coal	7,600.00	8.9	.147	.192
3. Fischer process, Europe design, natural gas at $0.05 per 1,000 cu. ft.	4,750.00	6.5	.06	.088
4. Modern high-pressure hydrogenation of petroleum	1,150.00	1.4	.048	.055
5. Modern oil refinery crude at $1.20 per bbl. thermal cracking	700.00	.7	.051	.053
6. Modern oil refinery crude at $2.00 per bbl. thermal cracking	700.00	.7	.083	.085

Items 1 and 2 are for plants of 2,950 bbl. and 3,960 bbl. production capacity/day, respectively. For larger plants, that is, 30,000 tons, the costs would be slightly lower, probably about $0.15–$0.16/gal. and $0.155/gal., respectively.

880. Farkas, A., and Farkas, L. Ortho-, Para- and Heavy Hydrogen. MacMillan Co., New York, 1935, 215 pp.

In certain cases a relationship is known to exist between magnetic properties and catalytic activity. For example, the conversion of *o*- and *p*-hydrogen is catalyzed by paramagnetic ions, the rate of conversion increasing with increasing magnetic moment of the ions. The so-called magnetocatalytic effect is based on similar phenomena.

Farkas, L. *See* abs. 880.

881. Farrar, L. D. Acres of Promise for Synthetic Fuels. Public Utilities Fortnightly, vol. 46, 1950, pp. 210–222.

Economy of the synthetic liquid fuel processes is discussed. The cost of H_2 constitutes about 50% of the total cost of liquid products from the Bergius process, while the cost of synthesis gas represents 60–70% of the total cost of Fischer–Tropsch products. Underground gasification of coal is being investigated as a lower cost method of producing gases suitable for both processes.

882. Farup, P. [Catalytic Influence of Ores on the Decomposition of Carbon Monoxide.] Tids. Kjemi Bergvesen, vol. 6, 1926, pp. 1–6, 15–17; Chem. Abs., vol. 21, 1927, p. 1243.

Catalytic decomposition of CO in the presence of Fe oxides has been studied experimentally at 400°–500°, the interval of maximum efficiency of this reaction. Pieces of different species of Fe ore, concentrates, and briquets were heated in a current of pure CO and the formation of CO_2 and C was observed and measured. Briquetted ore has a catalytic effect several times greater than that of fresh ores and concentrates. The burning temperature of the briquets could not be seen to have an influence upon the catalytic efficiency, nor was this considerably reduced in briquets burned with a small addition of $CaCO_3$ or NaCl.

883. Fast, E. Spectrographic Determination of Potassium in Iron Catalysts by Fractional Distillation. Anal. Chem., vol. 22, 1950, pp. 320–322.

Spectrographic method for determining K in Fe catalysts has been developed. K was found to distill quantitatively from a sample pellet during the initial arcing period. By photographing the spectrum during this period only, interference due to Fe was eliminated. The length of the log sectored K line was found to be a linear function of the log concentration of K. An average deviation of 5–10% of the amount present is indicated by repeated determinations on the same sample. Na and Li can be determined in the same manner. The method is not applicable to catalysts containing several percent of C.

884. Fauser, G. [Synthetic Gasoline.] Energia Termica., vol. 7, 1939, pp. 30–37.

Characteristics are given of the Fischer-Tropsch process for synthesis of gasoline from H_2 and CO and of catalytic hydrogenation under high pressure by the Bergius process. Data on world development in technique of hydrogenation and production of synthetic gasoline in Italy are given.

885. Federal Power Commission. Natural-Gas Investigation by the Federal Power Commission. Oil and Gas Jour., vol. 45, No. 8, 1946, pp. 60–61.

Abstract of testimony by P. C. Keith, president of Hydrocarbon Research, Inc., on the development of processes for making gasoline from natural gas and for gasifying and liquefying coal. (*See* abs. 1780.) Fuel reserves as of Jan. 1, 1946, if converted into crude oil, would make a total of 6.326 billion bbl. divided: 21 billion bbl. from crude, 25 billion from natural gas, and 6,280 billion bbl. from coal synthesis. It is predicated that commercial production of gasoline from natural gas and from coal will take place within 5 yr. Experiments had been made in the production of city gas from coal, and a gas had been obtained of 600–900 B. t. u. at a cost of $0.17/1,000 cu. ft. It is estimated that gas could be produced at West Virginia coal mines and transported to New York for $0.242/1,000 cu. ft. By this process 10,000 tons of coal would produce about 200 million cu. ft. of gas. It is also stated that gasoline can be made from coal for $0.06/gal., assuming the cost of coal at $2.00/ton. The time will probably come in the not too distant future when this price will be competitive with petroleum and natural gas.

886. ———. Prospects for Production of a Substitute for Natural Gas. Natural-Gas Investigation Docket G. 580, 1947; Chem. Eng., vol. 54, No. 8, 1947, pp. 104–106.

Four methods to manufacture high-B. t. u. gas from coal are described: Fischer-Tropsch hydrocarbon synthesis; pressure gasification and hydrogenation (Lurgi plant); coal hydrogenation with gas byproduct (Bergius process); underground gasification and catalytic enrichment. Each process is illustrated by flow charts. Economic factors are discussed.

Feditschkina, T. L. *See* abs. 803.

887. Fehling, H. R. Adiabatic Temperature and Equilibrium of the Gasification Process. Jour. Inst. Fuel, vol. 14, 1940, pp. 39–46; Chem. Abs., vol. 35, 1941, p. 3415.

Ideal gasification, wherein the reaction products are in thermodynamic equilibrium and no heat is lost, is illustrated by a diagram showing the interdependence of temperature, calorific value, steam saturation, and steam decomposition. It also shows the theoretical limits of the process. Analysis of experimental results with this diagram indicates that with low steam saturation nearly complete decomposition of CO_2 and H_2O is attainable. At saturation temperatures above 45° the reaction velocity sets a limit and prevents complete decomposition when the temperature falls below a critical point that depends chiefly on reactivity. Thermodynamic efficiency, as opposed to thermal efficiency, is defined as the degree of approach to the theoretical limit of a producer. Experimental results show that gas quality and thermal efficiency may be improved only by increasing the amount of steam in conjunction with more reactive fuels, preheating the air and steam, and providing special aerodynamic conditions. The so-called "wall effect" observed in producer practice is explained thermodynamically.

Feisst, W. *See* abs. 1042, 2874.

Feldman, J. *See* abs. 42a.

888. Feldman, J., Pantazoplos, P., Pantazoplos, G., and Orchin, M. Design, Construction, and Operation of a Distillation Laboratory for the Synthetic Liquid Fuels Program. Bureau of Mines Rept. of Investigations 4764, February 1951, 4 pp.

Detailed description, with numerous diagrams and figures, of the distillation laboratory at Bruceton, Pa., which was established to aid in the separation and identification of the products produced in the synthetic liquid fuel processes. Compounds present in synthetic liquid fuels may include aliphatics C_1–C_{∞} or greater. Alcohols, ketones, esters, aliphatic carboxylic acids, saturated hydrocarbons, olefins, and diolefins are all found in Fischer-Tropsch products. Coal hydrogenation products contain, in addition to aliphatic compounds, a large proportion of naphthenic material and aromatic compounds ranging from benzene to coronene; in addition, appreciable amounts of tar acids and bases are present. In designing the laboratory, provision had to be made for the greatest amount of flexibility and versatility. A great deal of standardization of basic equipment had also to be designed to permit interchange of parts and services.

889. Feldman, O. Synthesis of Petroleum. South African Min. and Eng. Jour., vol. 46, pt. 1, 1935, pp. 361–362; Chem. Abs., vol. 29, 1935, p. 7055.

Fischer process for the synthesis of liquid and solid hydrocarbons from CO and H_2 at atmospheric pressure and 200°–250° is described. The yields are gasol, b. 30°, 4% (50% olefins); gasoline, b. 30°–200°, 62% (30% olefins); oil, b. +200°, 23% (10% olefins); paraffin wax, m. p. 50°, 7%; and paraffin deposits, m. p. +70°, in catalyst, 4%.

890. Feldman, Y. A., and Allison, E. [Crude Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 1237–1240; Chem. Abs., vol. 30, 1936, p. 2170.

The lower boiling portion of the byproducts distilled from synthetic MeOH consists mostly of ethers and esters, of which MeOAc is the main representative. Me_2S, Me_2CO, and aldehydes are also present. About half the higher-boiling fraction is iso-BuOH. The rest consists of other higher alcohols and acids.

891. Feldman, Y. A., and Khaïkova, N. A. [Production of Synthetic Methanol from Water Gas.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 970-975; Chem. Abs., vol. 31, 1937, p. 240.

Corrosion in Fe apparatus is chiefly due to formation of $Fe(CO)_5$ by CO in the presence of H_2O, although S compounds are also harmful. Cr–V and Cr–Ni steels are also easily attacked by CO.

892. Feldman, Y. A., and Nikitin, V. M. [Use of Higher Alcohols Obtained in the Synthesis of Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 922–924; Chem. Abs., vol. 30, 1936, p. 7538.

Higher boiling fraction from synthetic MeOH is treated with 475–500 kg. of HOAc per ton of alcohols and 4–5% of the weight of HOAc of H_2SO_4 and refluxed for 1.5–2 hr. The MeOAc distilled off in yields of 1–20% up to 72°. Distillation is continued to 87°, yielding a mixture of iso–BuOH, iso–BuOAc, and H_2O. The H_2O is separated and the other components returned to the still and redistilled. In this way 40–60% of iso–BuOAc is obtained. The H_2O solution is salted out with 25% its weight of NaCl and gives 3–3.5% iso–PrOAc and iso–BuOAc.

893. Feldman, Y. A., Ivanov, K. N., and Naumova, A. I. [Use of Siderite as a Source for Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 1036–1038; Chem. Abs., vol. 30, 1936, p. 1190.

When Bakal siderite is fused without removing any impurities, most of the Fe_2O_3 becomes Fe_3O_4, and a good catalyst for NH_3 synthesis is obtained. Addition of Al_2O_3 or K_2O does not improve it.

894. Fenske, M. R. Unit Processes in Organic Synthesis, by P. H. Groggins. McGraw-Hill Book Co., New York, 3d ed., 1947, chap. VIII, pp. 488–562.

General discussion of hydrogenation with special emphasis on the following industrial applications: Hydrogenation or hardening of vegetable or marine oils; the synthesis of MeOH, higher alcohols, and hydrocarbons from water gas; the reduction of long-chain fatty acids to alcohols; hydrogenation of hydrocarbons, mineral oils, and coal.

———. *See* abs. 1098, 1099, 1100, 1104, 1105.

Fenske, M. R., and Frolich, P. K. Catalysts for the Formation of Alcohols From Carbon Monoxide and Hydrogen. V. Decomposition and Synthesis of Methanol With a Zinc-Copper-Chromium Oxide Catalyst. *See* abs. 1102.

895. Fergusson, R. R., and Barrer, R. M. Derivation and Development of Huttig's Multilayer Sorption Isotherm. Trans. Faraday Soc., vol. 46, 1950, pp. 400–407; Chem. Abs., vol. 44, 1950, p. 9768.

Statistical derivation is given of a generalized sorption isotherm based on evaporation-condensation properties of a sorbed molecule. Characterictic isotherm equations were obtained analogous to the various modifications of the Brunauer, Emmett, and Teller isotherm (abs. 389). Isotherms of types I, III, and to some extent V, are obtained but not types II and IV. A major objection to this and the Brunauer, Emmett and Teller treatment of multilayer sorption is the lack of interaction laterally with molecules in adjacent columns, although interaction with molecules in the same column is permitted.

896. Ferrero, P. [Chemical Evaluation of Coal.] Rev. univ. mines, vol. 9, 1933, pp. 453–458, 487–493; Chem. Abs., vol. 27, 1933, p. 5935.

Utilization of coal in the coking process and the products obtained by different processes are reviewed. Methods of obtaining aromatic substances, coloring materials, pharmaceutical products, explosives, CH_4, NH_3, HNO_3, HCN, different alcohols, formaldehyde, synthol, coke-oven gas, EtOH, acetone, and glycol are discussed and their reactions explained.

897. ———. [Present Chemical Syntheses Starting From Petroleum.] Rev. univ. mines, vol. 6, 1950, pp. 121–133.

Among other topics, the Fischer-Tropsch synthesis is discussed.

897a. ———. [Chemical Utilization of Gas Collected in Coal Mines.] Pubs. assoc. ing. faculté polytech. Mons, 1952, No. 1, pp. 74–78. Chem. Abs., vol. 46, 1952, p. 7736.

Many ways might be found to chemically utilize the gas (grisou) emanating in coal mines. Grisou contains 90% CH_4, 8% air, and small amounts of C_2H_4, H_2 and CO_2. Processes are reviewed for converting grisou to town gas and to synthesis gas for manufacture of NH_3 or MeOH by steam reaction in the presence of catalysts or by partial oxidation. Also mentioned are the manufacture of C_2H_2, HCN by various methods, chlorination, nitration, Oxo reaction, Fischer-Tropsch process.

898. Ferris, S. W. Limiting Compositions in Hydrocarbon Conversion. Ind. Eng. Chem., vol. 33, 1941, pp. 752–759; Chem. Abs., vol. 35, 1941, p. 7163.

Several investigators have attempted to show that the process of cracking hydrocarbons tends to approach an equilibrium. This term is not used in the present paper. Instead, attention is called to the tendency for a synthetic crude to be formed in the cracking reactions. The synthetic crude oil includes all the liquid material resulting from a reaction, under such conditions of condensation that vapor pressure approximates 10–15 lb./sq. in. From very different stocks the curves of distillation of the products of cracking are seen to approach a limiting band. The same tendency can be traced from the literature in catalytic as in thermal cracking, in destructive hydrogenation, alkylation, the Fischer-Tropsch synthesis from CO and H_2, catalytic reforming, and even in polymerization. The effect was similar when a naphthenic petroleum and successive synthetic crude oils from it were subjected to thermal cracking. The 3 passes after the 1st made little differences in the approach of the synthetic crude oils to the limiting band. It was found that if the distillation curve of the original stock lay to the right of the limiting band, the synthetic crude oil could not be forced to the left of it. Petroleums of this character were probably residual crude oils from which the light fractions had escaped in the course of geologic change. The petroleums whose distillation curves started at the left of the limiting band were regarded as distillate crude oils. If pyrolysis is pushed far enough, a 2d limiting composition can be detected in which benzene and napthalene predominate. This is a conclusion based on the data reported by Rittman, Dutton, and Dean. The conditions for the production of the limiting band depend upon an original specific gravity of 0.800–0.930. At higher specific gravities the available supply of H_2 is so limited that the tendency is toward benzene-naphthalene limiting composition.

899. Fester, G. [Catalytic Reduction of Carbon Monoxide.] Brennstoff-Chem., vol. 3, 1922, pp. 244–245; Chem. Abs., vol. 17, 1923, p. 1745.

An observation by Orlov has been confirmed, that is, that CO when reduced at 100° by H_2 in presence of a catalyst of Ni and Pd asbestos yields unsaturated hydrocarbons and not CH_4. The catalyst rapidly loses its activity.

900. Fester, G., and Brude, G. [Decomposition of Carbon Monoxide.] Ber. deut. chem. Gesell., vol. 56B, 1923, pp. 2245–2249; Chem. Abs., vol. 18, 1924, p. 1095.

It has been previously shown that the equilibrium $2\ CO \rightleftharpoons CO_2 + C$ (1) is displaced but slightly to the right at low temperatures for want of a suitable catalyzer (abs. 2219, 3001, and 3222), but that the equilibrium $CO + H_2O \rightleftharpoons CO_2 + H_2$ (2) in the presence of Pd black is displaced considerably to the right at low temperatures (abs. 3688). By using Pd adsorbed on active charcoal as catalyzer, CO, either alone or mixed with an equal volume of H_2, was decomposed at low temperatures in the presence of so small an amount of H_2O that reaction (1) took place and not (2). To prove that reaction (1) occurred, active charcoal was replaced by active SiO_2 whereby the free C formed in (1) was easily detected. By varying the amount of H_2O vapor present, H_2 in small or large amount was formed, owing to reaction (2). Contrary to Orlov (abs. 2532), no C_2H_4 could be detected in the products, though under certain conditions small amounts of saturated hydrocarbons and $Ni(CO)_4$ were detected.

901. ———. [Reactions of Carbon Monoxide.] Brennstoff-Chem., vol. 5, 1924, pp. 49–53; Chem. Abs., vol. 18, 1924, p. 2480.

During various attempts to reduce CO by H_2 catalytically, it has been observed that at low temperatures appreciable amounts of CO_2 are formed. A study is made of the formation of CO_2 from CO–H_2 mixtures and CO alone at temperatures 35°–240° with Pd precipitated on active C and on silica gel as catalysts. 2 reactions were considered: $2\ CO = CO_2 + C$ and $CO + H_2O = CO_2 + H_2$. Both were found to take place to a limited extent. Concentrations of 1 to 55% CO_2 in exit gases were obtained, the higher results being obtained at 240°, corresponding to 71% of the pure CO used. With CO : H_2 mixtures 1 : 1 the H_2 appeared to have no reducing action, presumably because of strong preferential adsorption of CO by active C and silica gel. Moist CO gave higher concentrations of CO_2, indicating that $CO + H_2O \rightarrow CO_2 + H_2$ took place. Preferential oxidation of CO in mixtures of H_2, O_2, and small amounts of CO with V_2O_5 as catalyst was tried without success, although with equal concentrations of CO and H_2, 2½ times as much CO as H_2 was oxidized.

Fetterly, L. C. *See* abs. 2441, 2442.

Field, J. H. *See* abs. 647, 648.

902. Fieldner, A. C. Gasoline Substitutes From Coal. Jour. Western Soc. Eng., vol. 31, 1926, pp. 306–315; Jour. Soc. Auto. Eng., vol. 20, 1927, pp. 98–104; Chem. Abs., vol. 20, 1926, p. 3557.

General review of the situation, and the status of research in the manufacture of gasoline substitutes from coal. 4 methods are described briefly and the physical and economic possibilities of each discussed: high-temperature carbonization; low-temperature carbonization; coal hydrogenation; and synthesis of alcohols from CO and H_2.

903. ———. Motor Fuel From Coal. Nucleus, vol. 4, No. 5, February 1927, pp. 20–25; Chem. Abs., vol. 21, 1927, p. 1175.

Approximate economic analysis is made of the Lander (low-temperature carbonization for production of smokeless semicoke and tar oils), Franz Fischer (synthetic hydrocarbons from water gas), Patart (catalytic synthesis of MeOH and higher alcohols from water gas under pressure), and Bergius (liquefaction of coal by direct hydrogenation at high pressure) processes for obtaining liquid fuels from coal under American conditions, to provide some basis for predicting when they may come into use for augmenting the supply of gasoline from petroleum. Low temperature carbonization is considered of minor interest, while the other processes cannot compete with petroleum gasoline until its refinery price rises to $0.30–$0.40 per gal.

904. ———. Use of Off-Peak Water-Gas Capacity for Methanol Production. Am. Gas. Jour., vol. 126, 1927, pp. 179–181; Chem. Abs., vol. 21, 1927, p. 1699.

An estimate based on data taken from a paper by G. Patart in the Proceedings of the International Conference on Bituminous Coal, 1926 (abs. 2589). The cost of production of MeOH by a large plant in the United States would probably be only $0.30 per gal., but the situation with regard to the use of off-peak water gas is less favorable.

905. ———. Recent Developments in the Production of Motor Fuels From Coal. Bureau of Mines Inf. Circ. No. 6075, 1928, 18 pp.; Fuel, vol. 7, 1928, pp. 492–501; Chem. Markets, vol. 23, 1928, pp. 375–378; Chem. Abs., vol. 23, 1929, p. 1245.

Review of the production of motor fuel by: (1) Carbonization of coal; (2) the Bergius process; and (3) the complete gasification of coal and conversion of the gases by pressure synthesis. It is believed that the Bergius process, or some modification of it, will prove most economical.

906. ———. Recent Developments in the Production of Motor Fuels From Coal. Canadian Chem. and Met., vol. 12, April 1928, p. 99.

Digest of a paper given before the Montreal Section of the Society of Chemical Industry. The 2 processes, Bergius and Fischer, are still in the semiexperimental stage, the former being about ready for actual commercial production and the latter still in the laboratory. It is predicted that the Bergius process will prove the more economical for motor fuel production from coal, while the synthesis of liquid fuels from gas will be limited to the utilization of byproduct gases and natural gas.

907. ———. Recent Developments in Coal Utilization. Synthesis of Chemical Products From Gases Produced From Coal or Coke. Bureau of Mines Minerals Yearbook, 1932–33, pp. 447–450; Chem. Abs., vol. 28, 1934, p. 284.

Production of gasoline by passing mixtures of H_2 and CO at atmospheric pressure over Fe or Co catalysts at approximately 260° C. has not reached commercial realization, although a semicommercial-scale plant at the Mülheim Coal Research Institute has been operating experimentally during the past few years. The earlier Co catalysts have been superseded by Ni-Mn-Al oxide on kieselguhr. This catalyst gave yields of 100–120 cc. of liquid products per m^3 of gas during 4 weeks of continuous operation. The yield had then decreased to 30% of the initial value. The catalyst must be regenerated by removing the accumulated paraffin. The maximum reaction temperature ranges from 190° at the beginning of a run to 210° C. at the end. The principal difficulties in large-scale commercial operation of the process are to dissipate the high heat of reaction and keep the catalyst at the proper temperature; also, the gases must be purified carefully to remove S. The solution of these problems is nearing completion.

908. ———. Developments in Coal Preparation and Utilization. Synthetic Hydrocarbons From Gases. Bureau of Mines Minerals Yearbook, 1934, pp. 627–643; Chem. Abs., vol. 29, 1935, p. 318.

At present, the production of synthetic motor fuel from gases does not have as good commercial prospects as production from coal or coal tar by hydrogenation.

909. ———. Recent Developments in Coal Preparation and Utilization. Bureau of Mines Minerals Yearbook, 1935, pp. 691–709; Fuel, vol. 15, 1936, pp. 173–179, 204–211.

Brief statement with bibliography of Fischer process for making synthetic products from gases.

910. ———. Recent Developments in Coal Preparation and Utilization. Bureau of Mines Minerals Yearbook, 1936, pp. 625–648; Fuel, vol. 16, 1937, pp. 160–176.

Review includes bibliography.

911. ———. Recent Developments in Coal Preparation and Utilization. Bureau of Mines Minerals Yearbook, 1937, pp. 935–954; Fuel, vol. 17, 1938, pp. 272–280, 300–307; Chem. Abs., vol. 31, 1937, p. 8062.

Review with extensive bibliography.

912. ———. Developments in Coal Research and Technology in 1937 and 1938. Synthetic Products From Gases. Bureau of Mines Tech. Paper 613, 1940, pp. 77–86; Chem. Abs., vol. 34, 1940, p. 7574.

Survey with bibliography. Economic data on the Fischer-Tropsch process are quoted from the Falmouth Committee report and the Labor Party Committee report with money, weights, and volumes converted into United States figures by G. Egloff. On the basis of these reports the cost for American conditions of synthetic gasoline would be about $0.14–$0.16 per gal.

913. ———. Production of Liquid Fuels From Coal and Lignite. Bureau of Mines Statement, Aug. 4, 1943; U. O. P. Co. Lib. Bull., No. 34, 1943.

Review of developments in the production of liquid fuels from coal by low-temperature carbonization, shale oil, and coal hydrogenation, both direct and indirect. It is estimated that the direct hydrogenation requirements for steel for plant and equipment are from 8.8–14.1 ton per bbl. of gasoline per day. Aside from the amount of steel, multi-stage compressors, special alloy-steel pressure vessels, and special electrical equipment would be required. The Fischer-Tropsch process does not need as much special equipment but must have more steel per barrel of gasoline, 8.9–14.3 tons.

914. ———. Production of Liquid Fuels From Coal and Lignite. Synthetic Liquid Fuels Hearings Before a Subcommittee of the Committee on Public Lands and Surveys, U. S. Senate, 78th Cong., 1st sess., on S. 1243, 1944, pp. 168–178.

Review of the production of liquid fuels by the Bergius coal hydrogenation and the Fischer-Tropsch synthesis processes. Estimated costs of production are taken from the paper by W. S. Farish (abs. 879). Bureau of Mines estimates for steel requirements differ somewhat from those stated in the above paper: 8.8 tons per bbl. of gasoline, as compared to 14.1 tons for a coal-hydrogenation plant; and 14.3 tons, as compared to 8.9 tons for a Fischer-Tropsch plant.

915. ———. Liquid Fuels From Sources Other Than Petroleum. Hearings Before a Special Committee Investigating Petroleum Resources, U. S. Senate, 79th Cong., 1st Sess., S. Res. 36, June 19–25, 1945, pp. 336–349; Nat. Petrol. News, vol. 37, No. 36, Sept. 5, 1945, R709, 711, 712, 714, 715.

Report made before the Senate Petroleum Investigating Committee on June 22, 1945, of the progress already made in the direct hydrogenation of coal and lignite; the conversion of coal, coke, natural gas, and other carbonaceous material to liquid fuels by the gas-synthesis process; and the recovery and refining of oil from shale. The early development and pilot-plant work is for the purpose of providing new and improved procedures for demonstration plants of up to 200 bbl. per day capacity. The program for the next fiscal year is summarized.

916. ———. Synthetic Liquid Fuels Program. Nat. Petrol. News, vol. 37, No. 36, Sept. 5, 1945, pp. R709, 711, 712, 714, 715.

Report before the Senate Petroleum Investigating Committee on June 22, 1945, of the progress already made in the direct hydrogenation of coal and lignite; the conversion of coal, coke, natural gas, and other carbonaceous material to liquid fuels by the gas-synthesis process; and the recovery and refining of oil from shale. The early development and pilot-plant work is for the purpose of providing new and improved procedures for demonstration plants of up to 200-bbl. per day capacity. The program for the next fiscal year is summarized.

917. ———. Nation's Reserve of Solid Fuels and Its Relation to the Future Supply of Gaseous and Liquid Fuels. Rept. to Federal Power Commission, June 1946, 12 pp.; Gas, vol. 22, 1946, pp. 70, 75, 78; Gas Age, vol. 98, No. 6, 1946, pp. 37–40, 42; Coal-Heat, vol. 50, November 1946, pp. 30–34; Mech. Eng., vol. 69, 1947, pp. 221–226, 228.

Reserves of mineral fuels in the United States are estimated as follows: Coal, 3.2 trillion tons; petroleum, 20.8 billion bbl.; natural gas, 135 trillion cu. ft. In terms of equivalent heating value, (coal taken at 13,000 B. t. u.), coal comprises 98.8% of the mineral-fuel energy reserves, oil shale 0.8%, petroleum 0.2%, and natural gas 0.2%. The coal reserves are distributed among the different ranks of coal on the basis of energy content in the following proportions: Anthracite, 0.6%; low-volatile bituminous coal, 2.2%; high-volatile bituminous coal, 54.2%; subbituminous coal, 23.1%; lignite 18.7%. The ultimate reserves of oil and gas are, therefore, very small as compared to the reserves of coal and lignite, and as the supply of oil and natural gas declines, it will be necessary to resort to coal either by direct substitution or by conversion of it to liquid and gaseous form. Fuel gases from coal by carbonization or complete gasification have been in commercial use for a long time, and recently processes have been developed for the conversion of coal to liquid fuel by the direct hydrogenation of coal or hydrogenation of tars or gases produced from coal. For coal hydrogenation by the Bergius process, most of the high-volatile bituminous coals, the subbituminous coals, and the lignites are suitable, while for the Fischer-Tropsch process, almost any carbonaceous material that can be reacted with steam to produce CO and H_2 is a potential source of liquid fuel. Furthermore it is not believed that the cost of producing liquid fuels by either of these processes will be in any sense prohibitive. From reports of German developments and from British and American estimates, it appears that, in general, gasoline can be produced by the hydrogenation of solid fuels for about $0.10–$0.15 per gal. more than from petroleum, and by the Fischer-Tropsch process for $0.06–$0.08 per gal. more.

918. ———. Synthetic Liquid Fuel Investigations of the Bureau of Mines. Science Counselor, vol. 10, No. 1, 1947, pp. 8–10, 24–26; Chem. Abs., vol. 41, 1947, p. 3937.

Survey including discussions of United States sources of supplementary liquid fuels, alcohol by vegetable fermentation, conversion of oil shale, liquefaction of coal or lignite by high-pressure hydrogenation, and conversion of water gas from coal or lignite; also European developments and their application to American conditions, synthetic gas production, and the cost of synthetic liquid fuels.

919. ———. Frontiers of Fuel Technology. Chem. and Eng. News, vol. 26, 1948, pp. 1700–1701; Fuel, vol. 28, No. 1, 1949, pp. 19–21.

Paper presented during the dedication of the Bureau of Mines synthetic fuels laboratories at Bruceton, Pa. It traces briefly the upward trend in the last 2 decades of new developments and improvements in the mining, preparation, and utilization of coal and predicts a new era in the processing of coal for the production of gaseous and liquid fuels. The basic German processes for the production of liquid fuels by coal hydrogenation and gas synthesis are already undergoing technical improvement toward a greater economy of operation in respect to American conditions.

———. *See* abs. 1370, 3121.

920. Fieldner, A. C., and Brewer, R. E. Tenth Annual Report of Research and Technologic Work on Coal for the Fiscal Year 1945. Electron-Microscope Studies of Fischer-Tropsch Catalyst. Bureau of Mines Inf. Circ. 7352, 1946, pp. 15–18; Chem. Abs., vol. 40, 1946, p. 5898.

Fischer-Tropsch catalyst consisting of Co–ThO_2–MgO–kieselguhr was studied by the electron microscope. Co oxide and several types of kieselguhr also were studied. A micrograph of the mixed catalyst shows the characteristic open structure of kieselguhr. Its effectiveness as a carrier is probably the result of this open structure, which permits the reacting gases to penetrate freely to the active components. The particles and aggregates are seen on the micrograph range in size from several microns down to 0.01 micron. Calculations from the effective surface area of this catalyst measured by an N_2-absorption method indicate that, if the material were composed of nonporous particles, their average diameter would be 0.015 micron. Apparently the larger particles are either aggregates of these very small ones or are porous enough so that gases can readily penetrate them. Since calculations of surface area from electron micrographs depend on the visually apparent particle size, such measurements obviously would not show the area effective in catalyzing the Fischer-Tropsch synthesis. Measurements made on a number of micrographs of the Co oxide gave an area of 4 $m.^2$ per gm., compared to 62 $m.^2$ per gm. obtained by the N_2 absorption method. For use in a proposed small-scale Fischer-Tropsch experimental plant, a CO generator was developed utilizing pitch coke or petroleum coke as fuel and having an O_2 blast. The raw gas leaving the generator contains approximately 97% CO, 1.6% N_2, 1% H_2 and 0.5% CO_2 and O_2. Most of the ash in the fuel is volatilized and is present in the gas as smoke necessitating electric precipitation methods for cleaning. Although the experimental unit had a capacity of 25,000 cu. ft. per day of CO, extension of the same principle to larger units seems warranted.

921. Fieldner, A. C., and Brown, R. L. Complete Utilization of Coal and Motor Fuel. Oil, Paint and Drug Reptr., vol. 108, 1925, pp. 12–13; Blast Furnace and Steel Plant, vol. 14, 1926, pp. 138–140, 148; Chem. and Met. Eng., vol. 32, 1925, p. 799.

Processes for obtaining motor fuel from coal may be grouped in 3 classes: (1) Carbonization of coal including gas manufacturing and low-temperature carbonization; (2) hydrogenation and liquefaction of coal by the Bergius process; (3) complete gasification of coal and conversion of the gases by pressure synthesis into MeOH, synthol, and other liquid combustibles.

922. ———. Comparative Study of Values Obtained in Synthesis of Methanol. Ind. Eng. Chem., vol. 20, 1928, pp. 1110–1112; Chem. Abs., vol. 22, 1928, p. 4461.

Values for the equilibrium constant in the Nernst equation have been calculated for the reaction: $CO+H_2=MeOH+Q$ calories, with the experimental data, which have been reported by different independent observers. In spite of probable variation in the exact conditions of the experiments from different laboratories, there is close agreement in the values of the constant.

923. Fieldner, A. C., and Fisher, P. L. Bibliography of Bureau of Mines Investigations on the Production of Liquid Fuels From Oil Shale, Coal, Lignite, and Natural Gas. Bureau of Mines Inf. Circ. 7304, 1945, 18 pp.

List of 236 refs. to papers written by the Bureau of Mines staff. (*See* abs. 1217.)

924. Fieldner, A. C., and Gottlieb, S. Thirteenth Annual Report of Research and Technologic Work on Coal, Fiscal Year 1948. Bureau of Mines Inf. Circ. 7518, 1949, 87 pp.

Summary of papers already published. The following subjects are noted: Electron-diffraction and electron-microscope studies of Fischer-Tropsch catalysts (p. 13); underground gasification of coal (pp. 71–73); production and purification of synthesis gas (pp. 73–76) and 4 diagrams; synthesis of liquid fuels from H_2 and CO, Oxo process, process mechanism, catalysts, internally cooled process (pp. 76–82); hydrogenation of coal, function of solvents and catalysts, Sn catalyst, hydrogenation of asphalt (pp. 83–86).

925. ———. Annual Report of Research and Technologic Work on Coal, Fiscal Year 1949. Bureau of Mines Inf. Circ. 7565, 1950, 97 pp.

This report, based largely upon publications issued during the fiscal year, summarizes research and technologic work of the Bureau of Mines on coal and coal products with continued emphasis on coking-coal reserves, conservation and mining safety, anthracite problems, and synthetic liquid fuels production.

926. Fieldner, A. C., and Schroeder, W. C. Oil and Gasoline From Oil Shale and Coal. Fuel, vol. 23, No. 2, 1944, pp. 34–36; Chem. Abs., vol. 38, 1944, p. 3445.

Review of processes with estimates of costs. The Fischer-Tropsch process offers a convenient means of converting natural gas to liquid fuel. In spite of the attractive possibilities, however, for the use of natural gas in this way, it is not desirable to encourage this development from the long-range national conservation viewpoint.

927. Fieldner, A. C., Beltz, J. C., and Fisher, P. L. Eighth Annual Report of Research and Technologic Work on Coal for 1943. Synthesis of Hydrocarbons From Water Gas. Bureau of Mines Inf. Circ. 7272, 1944, p. 56.

Experimental work on Fe and Co catalysts has been completed. Methods for the preparation and reactivation of Fe catalysts have been developed, and 1 Fe catalyst has been in operation for 3 months with no loss in activity. Fe catalysts yield a highly olefinic product and a larger proportion of solid paraffins than is obtained with the Co catalyst. Cheaper methods of preparation of Co catalysts have been investigated and a very promising method has been developed. Interpretation of available data on the steam-carbon reaction corroborates the generally accepted conclusions that the primary products are CO and H_2 and that CO_2 is formed subsequently by way of the water-gas reaction.

928. Fieldner, A. C., Ernst, F. A., and Brown, R. L. Use of Off-Peak Gas for Methanol and Hydrocarbon Synthesis, With Notes on the Bergius Process. Proc. Am. Gas Assoc., vol. 9, 1927, pp. 1031–1033.

Theoretical requirement of blue gas to make 1 ton of MeOH, with 70% conversion, is put at 100,000 cu. ft. A plant of 20-ton-per-day capacity will thus require 2,000,000 cu. ft. The total investment-per-ton-per-yr. for the gas plant plus the MeOH plant is calculated at $107.00–$128.00. On such a basis it is not considered that either MeOH or synthol could be produced to compete with gasoline as a motor fuel.

929. Fieldner, A. C., Fisher, P. L., and Brewer, R. E. Ninth Annual Report of Research and Technologic Work on Coal in 1944. Synthesis of Liquid Fuels by Hydrogenation of Carbon Monoxide. Bureau of Mines Inf. Circ. 7322, 1945, pp. 75–79; Chem. Abs., vol. 40, 1946, p. 5897.

Critical discussion on the preparation and properties of metal carbides and the reaction mechanism between CO and Co or Fe or their oxides to form carbides was published. (*See* abs. 1434). The reaction is stated to be much too slow to account for the rate of synthesis of hydrocarbons by reduction of carbides with H_2 when a mixture of CO and H_2 is used. It is known that the presence of H_2 with CO markedly accelerates the formation of C, which appears to proceed by way of the metal carbide. Since Co is a much more active catalyst than Fe for the water-gas reaction and because the most active Fe catalysts catalyze this reaction to only a slight degree at temperatures below 300°, it appears probable that H_2O and CO_2 are primary products on Co and Fe catalysts, respectively. Although metal carbides are formed on both Co and Fe, there is evidence that the mechanism of the synthesis on Co catalysts differs from that on Fe catalysts. An investigation has been made on the correlation of the physical properties, particularly X-ray diffraction pattern and ferromagnetism, of Fe catalysts with their mode of preparation and activity. An analysis of published data shows that the reaction rate in the Fischer-Tropsch synthesis is directly proportional to the partial pressure of the synthesis gas and inversely proportional to that of the products. The retardation of the rate by the products is large enough so that only little advantage is obtained, so far as space-time yield is concerned, by increasing the operating pressure from 5 to 20 atm. Under a total pressure of about 1 atm., dilution of the synthesis gas with N_2 decreases the yield of liquid hydrocarbons per unit volume of gas but does not decrease the % conversion. In fact, such a dilution results in a conversion somewhat greater than would be calculated on the basis of a first-order reaction. Photographs illustrate some of the development work being accomplished. The type of converter used in the Ruhrchemie plants to regulate the heat-transfer problem is illustrated. The catalyst is packed in narrow spaces between steel sheets through which cooling tubes are interlaced. Water under pressure is circulated through the tubes. The cost of such a converter is relatively high because of the large amounts of steel used per unit of oil produced. A promising method of removing the heat of reaction has been tested by the Bureau. It consists of flushing a cooling oil of proper boiling range over the catalyst particles, the heat of vaporization of this oil being supplied by the heat of the synthesis reaction. It has been found possible to maintain virtually complete adiabatic conditions in the converter, and precise temperature control has been readily obtained.

930. Fieldner, A. C., Gauger, A. W., and Yohe, G. R. Gas and Fuel Chemistry. Ind. Eng. Chem., vol. 43, No. 5, 1951, pp. 1039–1048.

Outline study of the development and growth of gas and fuel chemistry over the past 75 years or of the active initiation of the synthetic liquid fuels program by the Bureau of Mines.

931. Filhol, J. [Petroleum and Substitute Motor Fuels.] Sci, et ind., Tech. ind. pétrole, No. 284 bis, 1939, pp. 110–112; Chem. Abs., vol. 33, 1939, p 7531.

World petroleum production and consumption is reviewed along with French laws favoring (1) vehicles provided with gas generators or compressed gas, (2) those driven electrically, (3) products derived from bituminous schists, (4) alcohol fuels, (5) synthetic fuels, such as those produced by hydrogenation, and (6) benzene.

Fingas, E. *See* abs. 2436.

Fink, W. L. *See* abs. 424.

932. Finkelshtein, V. S., and Rubanik, M. Y. [Kinetics of Ammonia Synthesis by Technical Iron Catalysts.] Jour. Phys. Chem. (U. S. S. R.), vol. 6, 1935, pp. 1051–1058; Acta physicochim. U. S. S. R., vol. 3, 1935, pp. 945–956; Chem. Abs., vol. 30, 1936, p. 7286.

Apparent energy of activation of NH_3 formation was 21 cal. per mol. Considering the various reaction energies required, it seems that the primary step in NH_3 synthesis is not nitride but imide formation by direct union of N and H.

933. Finzel, T. G. Pyrophoric Iron. I. Preparation and Properties. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 142–149; Chem. Abs., vol. 24, 1930, p. 1275.

Pyrophoric Fe can best be prepared by the reduction of Fe_2O_3 in H_2 at 500° for 3 hr. The Fe_2O_3 was precipitated from Fe $(NO_3)_3$ solutions of different concentrations to produce oxides of different degrees of dispersion, which, in turn, would influence the pyrophoric activity of the reduced Fe. The pyrophoric Fe was inactivated by heating in H_2, N_2, or He. Oxides of the highest degree of dispersion yield pyrophoric Fe most easily inactivated—the ease of inactivation depending upon the degree of dispersion. The time factor of inactivation for the different gases varied in the order: $He > N_2 > H_2$. Inactivation is accompanied by a decrease in total surface. Samples were produced that displayed pyrophoric activity at −78° and in air that had been thoroughly dried.

934. ———. Pyrophoric Iron. II. Adsorption of Carbon Dioxide and Ammonia and the Use of Pyrophoric Iron in the Ammonia Synthesis. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 150–156: Chem. Abs., vol. 24, 1930, p. 1275.

Relations between pyrophoric activity and adsorptive and catalytic properties were investigated. Adsorption of CO_2 by pyrophoric Fe is no criterion for pyrophoric activity; adsorption seems to depend primarily upon the amount of residual oxide contained in the Fe. Sensitivity and ease of inactivation of pyrophoric Fe may be due to rapid recrystallization, the processes of which are hindered by the presence of cores of Fe_2O_3 in the particles. Fe prepared from colloidal Fe_2O_3 is worthless as a catalyst in the synthesis of NH_3.

935. Firsanova, E. N. [Chemical Composition of Synthin. I.] Khim. Tverdogo Topliva, vol. 8, 1937, pp. 892–901: Chem. Zentralb., 1938, II, p. 1523; Chem. Abs., vol. 32, 1938, p. 4308.

Products of the reaction of CO and H_2 in the presence of the catalysts Ni–Al, Ni–Co–Si and catalyst "*a*" (composition not disclosed) at 180°–200° were analyzed. The mixture of gasoline and oil can yield a product boiling up to 200° in amounts of 60%. The synthin consisted mainly of paraffin hydrocarbons with smaller amounts of unsaturated compounds and no naphthenes nor aromatic compounds, therefore, the synthin had a low antiknock value. The residue boiling over 250° contained 57% of solid paraffin. n–C_5H_{12}, C_6H_{14}, C_7H_{16}, C_8H_{18}, C_9H_{20}, $C_{10}H_{22}$ and $C_{11}H_{24}$ were found in the paraffin-hydrocarbon fraction. Iso compounds were not found in the fractions boiling up to 200°. No cycloolefins nor diolefins were found. 12 refs.

936. ———. [Investigation of the Chemical Composition of Synthin. II. Analysis of Water Formed in the Synthesis of Hydrocarbons.] Jour. Appl. Chem. (U. S. S. R.), vol. 18, 1945, pp. 367–371; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 589; Chem. Abs., vol. 40, 1946, p. 3246.

Results of this work show that the products of interaction of CO with H_2 under atmospheric pressure in the presence of a Ni–Co–Al catalyst at 180°–190° contain not only hydrocarbons and small amounts of acids but also aliphatic alcohols and aldehydes soluble in H_2O. From the reaction water 0.15–0.37% neutral oxygenated compounds have been isolated, for the most part alcohols. Methyl, ethyl, *n*–propyl, and *n*–butyl alcohols were isolated and identified; amyl alcohol also is present apparently. In addition to alcohols, an aldehyde was isolated but could not be identified. In contrast to literature data, only a small amount of acetone was found among the oxygenated compounds, about 2%. The acids isolated from the water and identified comprise acetic, propionic, and butyric. The presence of formic acid was shown by only a qualitative test.

937. Firth, F. G. X-ray Diffraction. I. Basic Principles and Theory. II. Constitution of Matter. III. Application of X-ray Diffraction. Petrol. Refiner, vol. 24, No. 4, pp. 114–120; No. 5, 1945, pp. 117–119; No. 6, 1945, pp. 111–114.

Brief statement as to its applicability to the study of Fischer-Tropsch catalysts.

938. Fischbeck, K., an Salzer, F. [Change of the Catalytic Effect of Metals at the Transition Point.] Ztschr. Elektrochem., vol. 41, 1935, pp. 158–169; Chem. Abs., vol. 29, 1935, p. 3958.

Sharp decrease of the catalytic activity with the change into the high-temperature form was shown for (1) the decomposition of NH_3 on Fe and (2) the hydrogenation of CO_2 on catalysts of Ni 5–Co 95%, and Ni 10–Co 90%. At the demagnetization temperature of Ni and Ni–Cu alloys, no discontinuous change of the catalytic activity was observed. They conclude that, per unit surface, the catalytic activity of 2 forms of the same substance is different.

939. Fischer, F. [New Possibilities of Obtaining Oil From Coal.] Ges. Abhandl. Kenntnis Kohle, vol. 4, 1919, pp. 458–470; Brennstoff-Chem., vol. 2, 1921, pp. 386–387.

Introductory remarks on the synthesis of oils from gas with special reference to the work already done by the Badische Co. and by Uhde. Occurrence of carbides as the intermediate product is discussed.

940. ———. Conversion of Coal Into Oils. Colliery Guard., vol. 128, 1924, pp. 87–88; Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 287–297; Ztschr. Ver. deut. Ing., vol. 69, 1925, pp. 15–17; Chem. Abs., vol. 18, 1924, p. 3470.

Address before the World Power Conference, including a discussion of destructive distillation in general, the hydrogenation of coal, and the synthesis of oils from gases.

941. ———. Umwandlung der Kohle in Öle. Berlin. Gebrüder Borntraeger, 1924, 367 pp.; Chem. Abs., vol. 19, 1925, p. 1622.

942. ———. Conversion of Coal Into Oils. Transl. by Lessing. D. Van Nostrand Co., New York, 1925, 284 pp.

Book has 5 chapters dealing, respectively, with the production of oil from coal by extraction with solvents, low-temperature carbonization, hydrogenation, synthetic processes, and by way of carbides. The 1st and last chapters are negligible, the other 3 making up the bulk of the book.

943. ———. Liquid Fuels From Water Gas. Ind. Eng. Chem., vol. 17, 1925. pp. 574–576; Chem. Abs., vol. 19, 1925, pp. 2119–2120.

Reactions with CO and various catalysts are discussed. Processes are developed for the formation of MeOH, and from this a mixture of alcohols is made called synthol. By heating synthol at 400° in an autoclave, there is formed synthin, a petroleumlike liquid, about ½ of which is saturated hydrocarbons similar to benzine or gasoline, the other ½ being soluble in concentrated H_2SO_4.

944. ———. [Methanol and Synthol Made From Carbon Monoxide as Motor Spirit.] Brennstoff-Chem., vol. 6, 1925, pp. 233–234; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 215–217; Chem. Abs., vol. 19, 1925, pp. 3361–3362.

Road tests were made with a 4-cylinder truck motor, 12-hp., 75-mm. bore, and 130-mm. stroke, the weight of the truck being 1,600 kg. Compression of the motor was raised from 4.6 to 6.0 atm. by change of pistons. Fuels used on the test were: (a) Pure MeOH, (b) national fuel (benzine: EtOH=1:1), (c) benzine with 20% kerosine and 2% lead tetraethyl, (d) benzine with 30% kerosine and 2% lead tetraethyl. Fuel required per 100 km., maximum speed on the level, and average speed, respectively, for the different fuels: (a) 22 l., 80 km. per hr. and 46 km.; (b) 11.6 l., 85 km. and 50 km.; (c) 12.7 l., 93 km. and 62 km.; (d) 11.7 l., 90 km. and 55 km. With pure MeOH and 6 atm. compression there was trouble from preignition without detonation; with 5% H_2O the MeOH ignited properly.

945. ———. [Coal Liquefaction and Complete Gasification.] Naturwissenschaften, vol. 14, 1926, pp. 1213–1214; Chem. Abs., vol. 21, 1927, p. 1342.

Short review without details of modern gasification processes. Purified water gas is treated with Fe or Co catalyzer at 200°–300° and atmospheric pressure. Benzine, petroleum, and paraffin formed are removed. The gas remaining has a heating value of 6,000–7,000 cal. per m.³ and is a valuable byproduct of the process.

946. ———. Synthesis of Petroleum. Nat. Petrol. News. vol. 18, No. 47, 1926, pp. 49–51; Chem. Age, vol. 15, 1926, pp. 610–611; Chem. Abs., vol. 21, 1927, p. 2182.

Progress of the hydrogenation of CO is discussed. The hydrogenation of CO under high pressure with an excess of H_2 produces O_2-containing compounds only. At pressures above 130 atm. and at temperature below 400°, MeOH only is formed when ZnO is used as a catalyst. Petroleum hydrocarbons are produced at ordinary pressure and 200°–300° temperature with finely divided Co and Fe as the catalyst. The process may be so conducted that in addition to higher hydrocarbons, the uncondensed gases have the proper ratio for further reaction after the removal of CO_2. The product most simply produced is gasol, a mixture of C_2H_6, C_3H_8, and C_4H_{10}. In order to produce gasoline it is necessary to achieve a nice balance in the catalyst because the polymerization tends to go on to the formation of solid paraffins, especially when strong bases are used. A yield of 100 gm. of solid liquid and liquefiable hydrocarbons can be obtained from each m.³ of water gas which is led several times over the catalyst. The theory of the process indicates that intermediate carbides are formed that react with H_2 and CO.

947. ———. Synthesis of Petroleum. Proc. Internat. Conf. Bituminous Coal, 1st Conf., 1926, pp. 234–246; Chem. Abs., vol. 21, 1927, p. 2378.

General review and discussion of the synthesis of hydrocarbons from water gas.

948. ———. [Chemistry and Coal.] Brennstoff-Chem., vol. 8, 1927. pp. 226–231; Ztschr. angew. Chem., vol. 40, 1927, pp. 799–804; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 415–425; Chem. Abs., vol. 21, 1927, p. 3116.

Lecture touching upon the development of coal hydrogenation and the production of hydrocarbons by synthesis from water gas.

949. ———. [Progress in the Field of Chemical Gas Purification and Conversion, Particularly With Reference to the Production of Synthetic Products From Gases.] Brennstoff-Chem., vol. 8, 1927, pp. 221–225; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 439–449.

950. ———. [Synthesis of Petroleum Hydrocarbons.] Brennstoff-Chem., vol. 8, 1927, pp. 1–5; Fuel, vol. 6, 1927, pp. 89–94; Proc. Internat. Conf. Bituminous Coal, 1st Conf. 1926, pp. 234–246; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 384–393; Canadian Chem. and Met., vol. 11, 1927, pp. 7–10; Fuel Econ., vol. 2, 1927, pp. 335–338, 616–617; Chem. Abs., vol. 21, 1927, p. 1537.

Refers briefly to recovery of hydrocarbons from coal by low-temperature carbonization and by hydrogenation under pressure, Bergius process. The last process carried out at 200 atm. and 400°–500° converts about half the coal into oil. Hydrogenation of CO may be carried out at both high and low pressures. At high pressures with an alkalized Fe catalyst, a mixture of acids, alcohols and aldehydes is obtained (synthol, abs. **101, 944, 3198**); with a ZnO catalyst MeOH is obtained. At atmospheric pressure with Fe metals as catalysts, hydrocarbons (abs. **1018, 1020, 1021**) from butane to solid paraffin are obtained. Co is more active than other metals of the series; the temperature should be 200°–300° and the ratio H_2 : CO about 1 : 1. Temperatures higher than 300° favor CH_4 formation; strong bases in the catalyst favor solid paraffin. A yield of 100 gm. of liquids was obtained by several passages of the gas. Water gas may be used, but it must be especially purified and freed from organic S. With pure gas the catalyst retains its activity indefinitely. Fischer proposes to use his process as an adjunct to water-gas plants where it can be used to produce motor spirit or to enrich gas for distribution as required.

951. ———. [Twelve Years of Coal Investigation.] Ztschr. angew. Chem., vol. 40, 1927, pp. 161–165; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 338–348; Chem. Abs., vol. 21, 1927, p. 1340.

Review of the researches conducted on the hydrogenation of coal and water gas.

952. ———. [Formation at Relatively Low Temperatures of Carbides Yielding Acetylene.] Brennstoff-Chem., vol. 9, 1928, pp. 328–333; Chem. Abs., vol. 23, 1929, p. 2662.

BaC_2 is prepared from BaO by heating with C in an electric porcelain-tube furnace in a stream of CH_4, with or without the addition of a small quantity of Fe_2O_3 and CaO. BaC_2 yielding 60% of the theoretical C_2H_2, was obtained by heating a mixture of 2 gm. BaO+1 gm. CaO+0.2 gm. Fe_2O_3 for 30 min. at 1,150° in CH_4 at 35 mm. pressure. Carbides were not formed below 850° and yields fell sharply above 1,150°. The highest yields were obtained in an atmosphere of CH_4. The carbide formed at these low temperatures yields both H_2 and C_2H_2 with H_2O. Fischer believes that free Ba is first formed by reduction, and this is partly converted into BaC_2 and partly into BaH_2.

953. ———. Formation of Benzene and Hydrocarbons by the Action of Heat on Methane. Chem. Markets, vol. 23, 1928, pp. 587–591; Chem. Abs., vol. 23, 1929, p. 1119.

By conducting CH_4 of various origins through tubes at certain temperatures, pressure, rate of flow, and cooling speeds, it was shown that C_6H_6, $C_{10}H_8$, and other aromatic hydrocarbons could be formed, whereas earlier investigators had pointed to the formation of C (carbon black) and H_2 as the chief or only products. Experimental conditions and results are detailed, and the suggestion is made that in some countries where carbon black is now made by wasteful processes it may be feasible to resort to CH_4 as raw material for synthesizing C_6H_6.

954. ———. [Synthesis of Aromatic Hydrocarbons From Methane at Atmospheric Pressure and Without Catalysts.] Brennstoff-Chem., vol. 9, 1928, pp. 309–316; Chem. Abs., vol. 23, 1929, p. 2694.

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

955. ———. [Solved and Unsolved Problems in Coal Investigation.] Brennstoff-Chem., vol. 10, 1929, pp. ~~444–447~~; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 450–459; Chem. Abs. vol. 24, 1930, p. 2859.

Chemical and biological problems encountered in the study of coal constitution are touched upon, and work on the complete gasification of coal is mentioned. The ideal here, not yet realized, is practical conversion of coal into O_2-free (except for CO) combustible gases. Recent research at Mülheim has aimed at complete technical purification, mainly desulfurization, of water gas and catalytic conversion of this into liquid hydrocarbons. Considerable work also is being done on the re-forming of fuel gases.

956. ———. [Development of the Benzine Synthesis From Carbon Monoxide and Hydrogen at Atmospheric Pressure.] Brennstoff-Chem., vol. 11, 1930, pp. 489–500; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 501–533; Chem. Abs., vol. 25, 1931, p. 796.

Motor benzine, colorless, S-free, and requiring no further refining, has been prepared on a semicommercial scale from industrial-gas mixtures, containing CO and H_2, in a train of apparatus consisting of purifiers, heaters, contact units, etc. Gas liquefaction has been increased from 20 to 50% with a Co–Cu–Th catalyst, and the possible use of a cheaper Ni catalyst is indicated. From 1 m.³ of a mixture of CO–H_2–C_2H_2, prepared by incomplete combustion of CH_4 and O_2, as much as 100 cc. benzine and 50 cc. oil have been obtained. The apparatus is shown schematically and detailed drawings are given of a number of the various designs of contact units employed in the tests. Questions involved in commercial utilization of the process with reference to necessary costs and feasible mixtures of coal, water, fuel, producer, and blast-furnace gases for use in the synthesis are discussed. A boiling-point composition curve for the benzine is given, together with a bibliography for 1926 to date.

957. ———. [Origin of Petroleum.] Brennstoff-Chem., vol. 11, 1930, pp. 352–354; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 583–594; Chem. Abs., vol. 25, 1931, p. 476.

Recent work and its relation to theories of inorganic and organic origin and secondary formation from fossil matter are discussed. It is postulated that under certain favorable conditions, synthetic petroleum could be produced from subterranean gases having the correct ratio of CO : H_2 through contact of steam with glowing C and catalyzed by Fe or alkaline earths.

958. ———. [Ruhr Coal as a Chemical Raw Material.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 724–730; Chem. Abs., vol. 26, 1932, pp. 3899.

959. ———. Utilization of Coal by Conversion to Gases. Jour. Indian Chem. Soc. Prafulla Chandra Ray Commemoration, vol., 1933, pp. 331–362; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 655–681; Chem. Abs., vol. 27, 1933, p. 5513.

Review of research and development on production of liquid fuel by benzine, synthol and MeOH synthesis.

960. ———. [Naphtha Synthesis From Water Gas for the Supply of Germany with Fuels.] Oel u. Kohle Erdoel Teer, vol. 11, 1935, pp. 782–785; Chem. Abs., vol. 30, 1936, p. 3968.

Process and the types of products obtained are briefly described.

961. ———. [Synthesis of Fuels and Lubricating Oils From Carbon Monoxide and Hydrogen.] Oel u. Kohle, vol. 11, 1935, pp. 120–123; Jour. Inst. Petrol. Technol., vol. 21, A, 1935, p. 170.

Hydrogenation of CO in the presence of Co, Ni, and Fe catalysts is first discussed. The maximum reaction temperature for the 1st 2 catalysts is 180°–200°, and for Fe 230°–250°; lower temperatures are required when the concentration of H_2 is high. The heat of reaction, unless controlled, favors the production of CH_4. A mixture of CO and H_2 is obtained from the gasification of coke. The proportion of the 2 gases should be 1 : 2. The mixed gases freed from S are brought into contact with the catalyst under suitable conditions, and about 100–120 gm. of liquid hydrocarbons (Kogasin) are formed per m.³ of gas. The fraction up to about 200°, termed Kogasin I, is of low octane number (47); that above 200°, Kogasin II, contains wax and after removal of the latter forms a satisfactory Diesel fuel. The separated wax has a melting point of 50°–60°. Kogasin II may be cracked to give a higher yield of low boiling constituents of high octane value. Alcohols may be obtained indirectly from the unsaturated hydrocarbons. No lubricating oils occur naturally in Kogasin, but they may be synthesized by a number of processes, including condensing the fraction rich in olefins with $AlCl_3$ and chlorinating high-boiling fractions and condensing the product with activated Al or aromatic hydrocarbons. The oils formed are resistant to oxidation, of low C residue, and of low pour point.

962. ———. [Synthesis of Fuels (Kogasin) and Lubricants From Carbon Monoxide and Hydrogen at Ordinary Pressure.] Brennstoff-Chem., vol. 16, 1935, pp. 1–11; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 334–356; Petrol. Refiner, vol. 23, 1944, pp. 70–76; Chem. Abs., vol. 29, 1935, p. 1959; vol. 38, 1944, p. 1621.

Work on the benzine synthesis begun in 1925 is completely reviewed. The conversion of CO or CO_2 by H_2 to liquid hydrocarbons depends upon the nature of the catalysts as well as the composition of the gas and the temperatures. The best catalyzing agents are Fe, Co, and Ni, each of which has the property of forming carbides, the splitting up of which is responsible for the formation of liquid hydrocarbons. With Co the reaction proceeds as follows: $CO+2H_2=(CH_2)+H_2O$ at a temperature of 180°–200°; with Fe $2CO+H_2=(CH_2)=CO_2$ at 250°. The pure metals are not used as catalysts, the conversion being promoted best by mixed catalysts, the composition of several of which is given together with some data as to their efficiency. In general, the yields obtained per m.³ of synthesis gas are 100–120 gm., as compared with the theoretical yield of 180 gm. Considerable is said about the heat of reaction and its disposition, the preparation of synthesis gas from coke and other gases, the primary products of the synthesis, their properties and uses, and their further conversion to alcohols and lubricants.

963. ———. Conversion of Coal Into Liquid Fuels by the Fischer Process. Petrol. Times, vol. 36, 1936, pp. 613–614; Chem. Abs., vol. 31, 1937, p. 1983.

Tropsch and Fischer (abs. **1018**) found that $CO+H_2$ at 400° and 100 atm. with alkaline Fe catalyst produced oxygenated hydrocarbons. At lower pressures less O_2 combines. A catalyst was developed, active at 190° and 1 atm., producing the paraffinic hydrocarbons Kogasin. Steam + CH_4 produces water gas containing 1 part CO to $2H_2$. The gas reacts over the catalyst with dispersion of heat, and the products are recovered by condensation and adsorption. The weight, percent, of products are: Gasol, 8; motor spirit, 62; diesel fuel, 24; paraffin wax, 2; and ceresin, 4, varying with operating conditions. The higher-boiling motor spirit requires treatment to improve antiknock properties; the diesel fuel is of the best type.

964. ———. Conversion of Coal Into Liquid Motor Fuels and Other Products by Way of Carbon Monoxide. Colliery Guard., vol. 153, 1936, pp. 719–721; Chem. Abs., vol. 31, 1937, p. 239.

Review.

965. ———. Motor Fuels From Coke by Way of Carbon Monoxide. Gas Jour., vol. 216, 1936, pp. 278–279; Jour. Inst. Fuel, vol. 10, No. 49, 1936, pp. 10–14; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 568–576; Chem. Ind., vol. 40, 1937, pp. 33–35; Ind. Chemist, vol. 12, 1936, pp. 483–484; Chem. Age, vol. 35, 1936, pp. 353–355; Engineering, vol. 142, 1936, pp. 481–482; Machinery Market, 1936, pp. 921–922, 942; Chem. Abs., vol. 31, 1937, p. 238.

Production of motor fuels from coal or coke by way of CO is described. Monoolefins have been found in the product and can be converted by addition of a few % of $AlCl_3$ into lubricating oils.

966. ———. Conversion of Coal Into Liquid Fuels by the Fischer Process. Chem. Inds., vol. 40, 1937, pp. 33, 35.

Review.

967. ———. [Synthetic Motor Fuels.] Osterr. Chem.-Ztg., vol. 40, 1937, pp. 159–162; Chem. Abs., vol. 32, 1938, p. 3121.

Lecture.

968. ———. [Hydrocarbon Syntheses in the Field of Coal Investigation.] Ber. deut. chem. Gesell., vol. 71A, 1938, pp. 56–67; Chem. Abs., vol. 32, 1938, p. 3329.

Summary of the investigations at the Kaiser-Wilhelm Institut für Kohlenforschung on the synthesis of C_2H_2 and C_6H_6 from CH_4 and of benzine and its homologs from CO and H_2.

969. ———. [Chemistry and Motoring.] Proc. 10th. Internat. Cong. Pure and Applied Chem., Rome, 1938, vol. 1, 1939, pp. 336–340; Brennstoff-Chem., vol 19, 1938, pp. 244–245; Forschungen u. Fortschr., vol. 14, 1938, pp. 239–241; Chem. Abs., vol. 32, 1938, p. 9435.

Lecture in which recent developments in production of motor fuels are briefly reviewed.

970. ———. [Present and Future Possibilities in the Production of Liquid Motor Fuels.] Brennstoff-Chem., vol. 22, 1941, pp. 2–7; Kraftstoff, vol. 16, 1941, pp. 378–9; Acqua e gas, vol. 31, March–April 1942, pp. 25–30; Chem. Zentralb., 1941, I, p. 2203; 1943, I, p. 1540; Chem. Abs., vol. 36, 1942, p. 3653.

Address reviewing briefly the many ways of producing liquid fuels.

971. ———. Middle Pressure Synthesis With Iron Catalysts. TOM Reel 49, July 13, 1943, frames 533–540; Bureau of Mines Transl.T–423, Dec. 1, 1947, 8 pp.

After presenting briefly the work of the Kaiser Wilhelm Institute on the middle-pressure synthesis with Fe catalyst, conditions are discussed that permit carrying out the synthesis at the lowest possible temperatures. Example: A synthesis gas CO : H_2=1 : 2 is converted at temperatures 200°–210° in several stages. The use of higher H_2 synthesis gas is particularly advantageous for the stability of the Fe catalyst. Using the Co middle pressure reactors for synthesis, the requirements may be met by using water gas as the synthesis gas. With a normal throughput (4 l. water gas per 10 gm. of Fe per hr.) the reaction temperature is about 220°, and it can be lowered to 210° with a reduced gas throughput.

972. ———. [Survey of Synthesis From Carbon Monoxide and Hydrogen.] Oel u. Kohle Erdoel Teer, vol. 39, 1943, pp. 517–522; Coke Smokeless-Fuel Age, vol. 5, 1943, pp. 208–210, 215; U. O. P. Co. Lib. Bull., Nos. 4–5, 1944; Chem. Zentralb., 1943, II, p. 1071; Chem. Abs., vol. 38, 1944, p. 949.

Historical survey. CH_4 synthesis, kogasin, isosynthesis (direct synthesis of high octane fuels), production of naphthenes and aromatics, production of MeOH and synthol, and direct production of fatty acids.

———. *See* abs. 1492.

973. Fischer, F. and Bahr, H. [Decomposition of Carbide-Containing Masses of the Iron Group by Acids, Water, or Hydrogen.] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 269–274.

974. ———. [Decomposition of Methane at Various Temperatures on Various Catalysts.] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 274–279; Chem. Zentralb., 1930, I, p. 31; Chem. Abs., vol. 25, 1931, pp. 2411–2412.

When a gas mixture rich in CH_4 (natural gas from Altengamme with 92.5% CH_4) was conducted through a heated quartz tube or through a heated porcelain tube, which was empty or filled with porcelain fragments, the decomposition started at 850° with deposition of C on the tube walls and with the formation of H_2, tar mist, and a slight quantity of small $C_{10}H_8$ crystals. When moist CH_4 is used, the quantity of the H_2 formed is almost twice that with dry CH_4 (34.3 : 19.1%). With finely distributed graphite as a catalyst, no tar and only very little $C_{10}H_8$ is formed. With $BaSO_4$ as a catalyst H_2O and H_2S are formed at 630°–650°; in this case also traces of an unsaturated hydrocarbon were noticed. The latter was also obtained when BaO was used. CH_4 is also decomposed when its presence in the gas current amounts to only 15%; in this case traces of C_6H_6 were noticed, which was identified as $PhNO_2$. When ZnO with addition of 1% K_2O in the form of K_2CO_3 was used, the CH_4 decomposition began at 700°; at 850° the increase in volume of the gas was 50.9% and remained the same when the velocity of the current was reduced from 2–5 l. per hr. to 0.5 l. per hr., but it was considerably lessened when the velocity of the current was increased to 6 l. per hr.

975. ———. [High-Carbon Carbides of the Iron Group.] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 255–269; Chem. Abs., vol. 25, 1931, p. 2932.

When CO is passed at 270° over finely divided Co or CoO, a mass is obtained that appears to contain the carbide Co_3C_2. This substance is decomposed by H_2 at 270°, half the C (presumably derived from the carbide Co_3C) being evolved as CH_4. Similar addition of C to an equimolecular mixture of CuO and Fe_2O_3 affords the carbide Fe_3C_4 in addition to Fe carbonyl. H_2 liberates CH_4 in proportion corresponding with the formula Fe_2C, formed apparently by separation of C from the unstable carbide Fe_3C_4. Small quantities of hydrocarbons are also formed. The Fe, but not the Co, carbide affords, when treated with acids, a mixture of hydrocarbons.

976. ———. [Reaction of Methane and Lower Homologs With Carbon Monoxide and Dioxide on Various Catalysts.] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 279–281; Chem. Zentralb., 1930, I, p. 31; Chem. Abs., vol. 25, 1931, p. 2411.

Repetition of Berthelot's experiment in which C_3H_6 was formed when 1 vol. CO and 2 vol. CH_4 were conducted through a glowing glass tube filled with pumice, yielded the same phenomenon. It was impossible to identify the hydrocarbon on account of the small quantity obtained. In another experiment, the same mixture of CH_4 and CO was conducted over various catalysts at different temperatures. CO was decomposed with formation of CO_2, CH_4 dissociated partly into C and H_2, but a reaction between CH_4 and CO was scarcely detectable. When the waste gas from a catalyst for the synthesis of mineral oil was conducted over metallic sponge Fe at 900°, the greatest part of the CO_2 was reduced to CO; gasol, heavy hydrocarbons, and a fraction of H_2 disappeared, and a large quantity of H_2O was formed.

977. Fischer, F., and Bangert, F. [Formation of Carbides Decomposable by Water From Manganese Oxide and Methane at Relatively Low Temperatures.] Brennstoff-Chem., vol. 10, 1929, pp. 261–265; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 694–706; Chem. Abs., vol. 24, 1930, p. 3453.

An excess of CH_4 was passed over pulverized oxide (MnO_2 or Mn_3O_4) heated to 800°–1,000°, both with and without admixture of other metallic oxides. Carbides formed were decomposed by H_2O and by HCl, and the hydrocarbons resulting were measured and analyzed. Of the admixed oxides, BaO and Al_2O_3 alone favored formation of carbides decomposable by H_2O. Formation of carbides decomposed by HCl was favored by NiO, Cr_2O_3, and Fe_2O_3. CeO_2, CaO, TiO_2, CuO, V_2O_5, and K_2CO_3 exerted little or no influence. The following are conclusions reached: (1) Carbides are formed by passing CH_4 over the Mn oxides at 800°–1,000°; (2) admixtures of foreign oxides strongly affect the properties of the carbides formed; (3) in the absence of heavy metal oxides, the Mn oxides heated to 800° and above in CH_4 give a carbide that will yield 90% of its C as gaseous hydrocarbons on decomposition with H_2O; (4) existence of a previously unknown Mn carbide $(Mn_3C_2)x$ is indicated.

978. Fischer, F., and Dilthey, P. [Preparation of Pure Carbon at Low Temperatures.] Brennstoff-Chem., vol. 8, 1927, pp. 388–391; vol. 9, 1928, pp. 24–30; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 234–255; Chem. Abs., vol. 22, 1928, p. 2641.

C is prepared by passing CO with H_2 (abs. 3580) over reduced alkalized Fe_2O_3 at temperatures around 500°. The catalyst is prepared by moistening 10 gm. Fe_2O_3 with 1 cc. water glass +15 cc. H_2O and painting this on an Fe spiral made from a strip of Knepp soft sheet 70 x 4 cm. This was heated in an Al retort similar to that used for low-temperature assay of coal, the preheated supply gas passing in at the bottom and out at the top of the retort chamber. A contact mass of this size, active Fe 6.8 gm. Fe_2O_3, will take gas at about 40 l./hr. and give 47% of the theoretical yield of C. The yield falls off in time, possibly because of conversion of active Fe_3C into higher inactive carbides. S is a contact poison; both the gas and Fe used must be free from S. A used contact mass could be repeatedly regenerated by dipping into 5 *N* KOH. The optimum temperature for CO reduction was 480°–490°, and the optimum ratio CO : H_2=3 : 1 An apparatus is shown for moderately large-scale work in which the C formed can be renewed continuously. The form of C recovered was investigated by X-ray and chemical methods, but no definite conclusion was reached. Its reactivity was found to be high. This, however, diminished on removal of Fe.

979. ———. [Solubility of Gas Benzines and Gases in Paraffin Oil.] Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 305–306; Chem. Zentralb., 1929, II, p. 3265; Chem. Abs., vol. 24, 1930, p. 5994.

On agitating 2 cc. of paraffin oil with various gases it was observed that C_5H_{12}, CO_2, and CH_4 were soluble to a remarkable degree, while H_2, CO, air, and water gas were insoluble. Corresponding experiments with the reaction gas of an active benzine catalyst did not succeed in connecting the results with the contraction of the catalyst or with the gas analysis.

980. ———. [Effect of Different Carriers on the Synthesis of Benzine.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 501–511; Chem. Abs., vol. 25, 1931, p. 3807.

Satisfactory catalyst was prepared by depositing Fe and Cu (4 : 1) in the form of nitrates upon a suitable support. Fe alone was unsatisfactory, as

were Fe and Ag catalysts. The reaction was carried out in Fe tubes, but unless these were treated with 5 *N* HNO_3 the catalyst lost its activity. The contact materials lose activity by the accumulation of high-boiling substances, but neither extraction nor hydrogenation restored activity, which could only be achieved by combustion in a current of air. Pt and Ru on an asbestos support proved an unsatisfactory catalyst. The formation of unsaturated hydrocarbons was considered doubtful.

981. ———. [Influence of Organic Sulfur Compounds in the Water Gas on the Synthesis of Petroleum.] Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 512–513; Chem. Abs. vol. 25, 1931, p. 3806.

In the synthesis of paraffins from water gas at 270°, using a contact mass prepared from Pb carbonate and Fe oxide, the catalyst takes up S from unpurified gas. The contact material can be regenerated by oxidation with air. The water gas used for the synthesis must be completely freed from S compounds.

982. Fischer, F., and Jaeger, A. [Reduction of Carbon Monoxide by Hydrogen in Contact With a Heated Iron Spiral in a Hot-Cold Tube.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 68–74; Chem. Abs., vol. 21, 1927, p. 2550.

When an electrically heated Fe wire spiral was brought to red heat in a mixture of 15% of CO_2, 23% of CO, and 56% of H_2, contained at 120–150 atm. in an Fe autoclave surrounded by cold water, the pressure fell to 70–80 atm. and a gas mixture containing about 9% of CO_2, 40% of CO, 22–29% of H_2, and 15–19% of CH_4 hydrocarbons was formed. H_2O containing a considerable amount of formaldehyde was also produced, and solid C was deposited on the spiral. By heating the spiral more carefully, to about 620°, the H_2 disappeared almost completely, and a larger amount of saturated hydrocarbons was produced, together with much free C and an aqueous liquid of acid reaction containing formaldehyde. The results were practically identical if the Fe spiral was previously treated with alkali, except that the yield of formaldehyde appeared to be less.

983. Fischer, F., and Koch, H. [Chemism of the Benzine Synthesis and the Motor and Other Properties of Products Resulting Therefrom (Gas Oil, Benzine, Diesel Oil, Hard Paraffin).] Brennstoff-Chem., vol. 13, 1932, pp. 428–434; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 516–530; British Chem. Abs., 1933, B, p. 50; Chem. Abs., vol. 27, 1933, p. 2017.

Theories of hydrocarbon formation are discussed critically; the carbide theory of Fischer and Tropsch is believed most satisfactorily confirmed by experimental findings. Hydrocarbons higher than CH_4 are obtainable from CO_2–H_2 mixtures only when the intermediate reduction to CO takes place. These are also obtained when HCOOH and MeOH are passed over Cu-Ni catalyst. Catalytic formation of paraffins of high melting point and molecular weight, composition, and characteristics of synthesis products, and their behavior as motor and diesel fuels have been investigated. Bibliography.

984. ———. [New Developments in the Adaptation of Cobalt Catalysts to the Benzine Synthesis.] Brennstoff-Chem., vol. 13, 1932, pp. 61–68; Ges. Abhandl. Kenntnis Kohle, vol. 10, 1932, pp. 556–577; British Chem. Abs., 1932, B, p. 376; Chem. Abs., vol. 26, 1932, p. 2582.

By increasing the activity of Co catalysts, the yield of liquid hydrocarbons has been increased from 100 to 153 cc./m.³ of gas mixture or to 71% of the theoretical. As catalysts, Co+18% Th precipitated with K_2CO_3 and Co+15% Mn precipitated with Na_2CO_3 were equally effective when used on kieselguhr as carrier. The influence of various precipitating agents in catalyst preparation and the effect of varying the proportion of carrier to catalyst and to activator in the catalyst at various temperatures have been determined. The use of Cu as activator for the Co resulted in lower reduction temperatures in the preparation of the latter by precipitation from the nitrate. Such catalysts, however, almost completely lost their activity at temperatures >350° and in H_2. Co catalysts have been used more than 2 months without interruption. Complete regeneration is effected simply by extracting the accumulated paraffins. In experiments to determine the reaction mechanism, the extent to which Co catalyst influenced the reaction $CO+H_2O \rightarrow CO_2+H_2$ was found strongly dependent upon reaction temperature. At 200° the effect was the same and at 235° much better than with Fe catalysts.

985. ———. [Synthesis of Lubricating Oils From Kogasin. Preliminary Communication.] Brennstoff-Chem., vol. 14, 1933, pp. 463–468; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 444–454; Petrol. Refiner, vol. 23, 1944, pp. 260–266; British Chem. Abs., 1934, B, p. 133; Chem. Abs., vol. 28, 1934, p. 2513.

Series of chlorination products has been prepared from the olefin-containing gas-oil fraction, Kogasin II, obtained in the benzine synthesis from CO and H_2. They were condensed with a number of aromatic hydrocarbons by using $AlCl_3$. Best yields were obtained with the trichloro and tetrachloro compounds and xylene. The oils resembled napthene-base oils in properties. Catalytic hydrogenation gives a water-white oil of low specific gravity, high stability against oxidation, and small carbon residue, which retains its lubrication value at low temperature. Comparative physical data are given for the various oils prepared. Bibliography.

986. ———. [Catalytic Hydrogenation of Carbon Disulfied at Ordinary and Elevated Pressures.] Brennstoff-Chem., vol. 19, 1938, pp. 245–249; Chem. Abs., vol. 32, 1938, p. 9437.

Analogy to the hydrogenation of CO_2 has been studied. Experiments at atmospheric pressure over Co catalyst at 170°–350° and at 184 atm. pressure at 305° with MoS_3 show complete conversions of a 1 : 3 mixture of CS_2 and H_2. In a 90% contraction with 4 l./hr. passage at 250°, H_2S and MeSH and Me_2S in a 3 : 1 proportion representing 80% of the CS_2 were formed. A maximum of 20% CH_4 was formed at 350° in 16 l./hr. passage of 1 : 5 CS_2–H_2 mixture. Separation of C was not observed nor was the formation of C_2H_4 established, although 1% of unsaturated hydrocarbons was noted in the 300°–320° tests. Strong exothermal fractions began at 190° in the steel autoclave with the 1 : 3 mixture with 30% CH_4 and H_2S. Slower hydrogenation at 200°–225° to 42 atm. was obtained with a 2 : 1 mixture, the balance of the H_2 being added subsequently, whereby no hydrocarbons were formed. The main liquid products then were a mixture of organic S compounds boiling 20°–150°, in which $(CH_2S)_3$ was identified with thioethers and mercaptans.

987. Fischer, F., and Küster, H. [Influence of Pressure and Temperature Upon the Synthesis of Benzine and Synthol in Liquid Medium.] Brennstoff-Chem., vol. 14, 1933, pp. 3–8; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 454–465; British Chem. Abs., 1933, B, p. 211; Chem. Abs., vol. 27, 1933, p. 2793.

Temperatures higher than those in the gas phase are necessary in the liquid phase because there can be no local spots of high temperature. Benzine yield is best at pressures near atmospheric. Synthol (alcohols, higher fatty acids, aldehydes, ketones, etc.) is formed at higher pressures. Describes apparatus. Bibliography.

988. Fischer, F., and Meyer, K. [Applicability of Nickel Catalysts to the Benzine Synthesis.] Brennstoff-Chem., vol. 12, 1931, pp. 225–232; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1932, pp. 534–555; Chem. Abs., vol. 25, 1931, p. 4685.

Effect upon yields of liquid products of adding various activators to Ni catalyst has been determined and is discussed at length. With Ni catalyst, it is possible to hydrogenate CO at atmospheric pressure and obtain products, of which ⅔ are liquids. As activator, 18% Th is used with the Ni in a 1:1 metal-kieselguhr mixture. The Th and Ni are precipitated by K_2CO_3 and are reduced with H_2 at 450°; addition of Cu does not serve to lower this reducing temperature. Addition of Mn appears, however, to increase the effect of the Th. The stability of the catalyst is such that only a 17% loss in yield was observed after 5 weeks' continuous use.

989. ———. [Activating Action of Ammonia Upon the Reduction and Activity of Nickel Catalysts.] Brennstoff-Chem., vol. 14, 1933, pp. 86–89; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 555–561; Chem. Abs., vol. 27, 1933, p. 3801.

Presence of NH_3 during the preparation of the catalyst increases subsequent yields in the benzine synthesis from CO and H_2. Reduction temperatures for maximum yields of fluid products are lowered from 450° to 300°–350°. Addition of NH_3 during the reduction, however, lowers the yields. Addition of 5% dry K_2CO_3 to the catalyst, prepared in presence of NH_3 to increase alkalinity, decreases its activity slightly. Impregnation with K_2CO_3 by solution almost completely removes activity.

990. ———. [Influence of Conditions of Preparation Upon the Efficiency of a Nickel–Manganese–Aluminum Catalyst.] Brennstoff-Chem., vol. 14, 1933, pp. 47–50; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 542–548; Chem. Abs., vol. 27, 1933, p. 3803.

Best yields in the benzine synthesis are obtained with 4–5 washings of the catalyst preparation. Lime water, instead of $CaCO_3$, as precipitant produces a nonuniform catalyst requiring more washing and giving poor yields. Previously described conditions for preparation still produce the best catalyst. Kieselguhr alone or with starch as supporting medium gave the best yields. Regeneration with H_2 in the presence of NH_3 gave the highest yield. Technical materials can be used in preparing the catalyst.

991. ———. [Reducibility of Standard Nickel Catalyst.] Brennstoff-Chem., vol. 14, 1933, pp. 64–67; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 549–554; Chem. Abs., vol. 27, 1933, p. 4034.

Reduction temperature of Ni–Mn–Al catalyst cannot be lowered by the addition of Cu in preparation or afterward as CuO or $CuCO_3$. Activity is, however, decreased by the former and increased by the latter method. CO–H_2 or 1:3 CO_2–H_2 mixtures cannot be used in place of H_2 for catalyst reduction, whereas 3:7 and 7:3 N_2–H_2 mixtures at 450° give normal activity.

992. ———. [Suitability of Alloy Skeletons as Catalysts for Benzine Synthesis.] Brennstoff-Chem., vol. 15, 1934, pp. 84–93, 107–110; Ber. deut. chem. Gesell., vol. 67B, 1934, pp. 253–261; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 356–382; British Chem. Abs., 1934, A, p. 389; Chem. Abs., vol. 28, 1934, p. 2871.

Catalysts prepared by Raney's method by dissolving Al or Si from alloys with Ni and Co are effective in hydrocarbon synthesis from water gas. The best results are obtained with a Ni–Co–Si alloy, in weight proportions of ½ : ½ : 1, from which the Si is removed as completely as possible with caustic soda. The effect of particle size, depth of catalyst, and depth of technical raw material is investigated. The activity of a mixed Ni–Co catalyst is decreased by Fe. With pure raw materials, the maximum yield of liquid hydrocarbons was 96 cc./m.^{3} of mischgas (23% CO and 46% H_2) and with technical material 80 cc. The addition of 10% Mn increased the yield with technical material to 88 cc. By increasing the amount of catalyst, the yield of liquid hydrocarbons can be considerably increased without cutting down the space velocity. With a mischgas containing 31.7% CO and 65% H_2, 161 cc. of liquid products could be obtained/m.^{3} of mischgas. Under special operating conditions, the space velocity can be increased 4-fold without any decrease in the yield. Addition of Cu decreases markedly the efficiency of Ni and Co alloys. By remelting catalysts poisoned by S with Si the original activity of the catalyst can be restored. The advantages and disadvantages of alloy skeletons are presented.

993. ———. [Use of Coke-Oven Gas for the Synthesis of Gasoline.] Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 497–500; Chem. Zentralb., 1934, II, p. 1061; Chem. Abs., vol. 29, 1935, p. 6747.

Coke-oven gas containing 5–6% CO is suitable for this synthesis with a Ni–Mn–Al catalyst. As a result of the ratio of H_2 : CO, which is higher than that of gas mixtures usually used for this synthesis, the reaction temperature must be reduced from 195° to 160°. The process is carried out so that a contraction of 20–25% is obtained, by which all of the CO but none of the CO_2 is used. In this way 20–22 cc. of hydrocarbons is obtained/m.^{3} of gas, of which 75% is gasoline. The heating value of the end gases is increased from 4,200 to 5,300 cal. Because of the S content of the gas, the reaction temperature must be increased slowly, 25° in 4 weeks, in order to compensate for poisoning of the catalyst. After this time, a complete reconditioning of the catalyst is necessary. The catalyst absorbs all the gaseous S.

994. Fischer, F., and Peters, K. [Decomposition of Methane, and Coke-Oven Gas in Particular, at Low Pressure by Electric Discharge.] Brennstoff-Chem., vol. 10, 1929, pp. 108–113; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 640–654; Chem. Abs., vol. 23, 1929, p. 4326.

Orienting experiments were made at atmospheric pressures and temperatures −185° to 750° wherein CH_4, coke-oven gas, and water gas were passed through a high-frequency-type ozone tube. Very little decomposition of CH_4 resulted, and the method was changed in that the discharge was passed directly through the gas maintained at low pressures, a Geissler-type tube of glass being used. The best conditions for decomposition of CH_4 were: pressure 40 mm. Hg, gas flow 367 l./hr., reaction tube diameter 35–60 mm., voltage drop between electrodes spaced at 40 cm. 5,000–7,000 v. room temperature. By starting with gas analyzing 2.8% CO_2, 1.5% illuminants (C_2H_2-free), 1.2% O_2, 5.4% CO, 52.3% H_2, 23.4% CH_4, and 13.4% N_2, a gas containing 8.5% C_2H_2, 67.7% H_2, and 4.8% CH_4 was obtained by one passage through the tube. The main reaction is considered to be $2CH_4 = C_2H_2 + 3H_2 - 4{,}000$ cal. About 15% of the energy supplied does useful work. Tar precipitated in the reaction tube is easily removed by passing water-gas or air through the tube, electric discharge being maintained. Experiments in which $C_{10}H_8$ was introduced into the reaction tube with H_2 and N_2 showed the reaction $C_{10}H_8 + H_2 + 5N_2 = 10HCN$ took place.

995. ———. [Influence of Electrical Discharge on Gas Containing Hydrocarbons at Diminished Pressure.] Ztschr. physik. Chem., Abt. A, vol. 141, 1929, pp. 180–194; Chem. Abs., vol. 23, 1929, p. 3861.

Discharge tube with steel electrodes, both cooled by incoming gas, was used. CH_4, both pure and distilled with H_2, was drawn through the tube. C_2H_2 was condensed with liquid air. Most of the CH_4 was converted to C_2H_2 and H_2. The influence of gas velocity, tube loading, and pressure are shown in tables. A pressure of 50 mm., gas velocity of 370 l./hr., and 1.3 kv.-a. power input gave 8.5% C_2H_2 in the exit gas, at an electric energy consumption of 31 kv.-a./m.^{3} C_2H_2.

996. ———. [Catalytic Gas Reactions in Liquid Medium.] Brennstoff-Chem., vol. 12, 1931, pp. 286–293; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 441–454; Chem. Abs., vol. 26, 1932, p. 24.

Results were similar when the catalyst was suspended in paraffin oil or methylnapthalene and when the catalyst was in contact with one of the liquid phases. Studies were made of hydrogenation and polymerization of C_2H_2 with Ni catalyst, formation of cuprene with Cu catalyst, hydrogenation of C_2H_4, formation of $Ni(CO)_4$, and formation of hydrocarbons from CO in a paraffin-oil medium with catalyst of Ni–Al–Th–kieselguhr (mol. ratio 1 : 1 : 0.4). The results are shown as follows:

Temperature, ° C.	CO, conv. percent	Products obtained, percent			
		CO_2	CH_4	C_2H_6	Higher hydrocarbons
175	7	2	-------	36	62
210	26	11	-------	26	43
250	72	20	32	18	30
270	75	30	44	10	16

Contact of the gas with the oil (about 20 sec.) was not sufficient for a quantitative conversion of the CO. The higher hydrocarbons contained relatively little unsaturated products and consisted chiefly of propane and butane when higher temperature was used, while at lower temperature the proportion of liquid hydrocarbons increased. Use of the catalyst in liquid media is advantageous for both laboratory and technical gas reactions, because it makes possible close control of temperature and eliminates overheating.

997. ———. [Electrical Formation of Hydrocarbons From Water Gas.] Brennstoff-Chem., vol. 12, 1931, pp. 268–273; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 586–597; Chem. Abs., vol. 25, 1931, p. 5853.

Method for quantitative conversion in gas reactions, especially exothermic, which in the glow discharge produce only low concentrations of reaction products. The apparatus consists of a discharge tube, operated with a relatively low charge, a freezing-out vessel and a Hg-vapor pump so connected as to permit recirculation of the reaction gas. It is possible to obtain corresponding electrical discharge equivalents for the condensable reaction products, which are removed continually. From CO–H_2 mixtures, various hydrocarbons are obtained in addition to CO_2 and H_2O. With liquid air for chilling, C_2H_2 and C_2H_6 predominate. At slightly higher freezing-out temperatures only higher hydrocarbons are recovered. The formation of CH_4 is believed to be the intermediate reaction, while traces of HCHO and MeOH are formed in the side reactions. When using water gas containing N_2, a 80–90% conversion of the N_2 into NH_3 and HCN takes place.

998. Fischer, F., and Philippovich, A. [Production of Formates From Carbon Monoxide and Bases in Presence of Water.] Ges. Abhandl. Kenntnis Kohle, vol. 6, 1921, pp. 366–381; Chem. Abs., vol. 18, 1924, p. 3170.

Percent yields of formate from different bases when 100 cc of a *N* solution, or suspension, of the base was heated, with shaking, with CO (88.7% purity) under 20 atm. for 1 hr. at 160° in an Fe autoclave, were as follows: KOH, 97.8; LiOH, 91.7; NaOH, 96.1; $Ca(OH)_2$, 92.3; $Ba(OH)_2$, 90.2; $Sr(OH)_2$, 84.8; NH_3, 15.3; calcined ZnO, 1.4; precipitated $Zn(OH)_2$, 3.5; $Zn(NH_3)_2(OH)_2$, 12.2; precipitated $Mg(OH)_2$, 4.4; $Fe(OH)_3$, 2.4; aniline, 0.2; low-temperature tar bases (boiling 250°–270°), 0.5; pyradine, 1.90; piperidine, 28.30. The reaction liquor contained Fe in all cases. With the weak bases, the yield of formate was increased by prolonging the time of heating. The rate of formation of HCO_2NH_4 at 100° was increased by the addition of HCO_2Na. From 11.09 *N* NH_3 solution by continued addition of CO under pressure at 160°–180°, 31.6% of formate was obtained, although partial hydrolysis apparently set in. The yield of formate was increased by the addition of $CaCO_3$ to neutralize the HCO_2H set free. Varying yields of formate were also obtained under similar conditions from hydrolyzable salts (Na silicate, borax, CaS, Na_2CO_3 and Li_2CO_3), Ca, Ba, and Mg carbonates, $Ca(HCO_3)_2$, Fe turnings, metallic oxides, and Na_2HPO_4.

999. Fischer, F., and Pichler, H. [Preparation of Hydrocarbons From Brown-Coal Coke at 500°.] Brennstoff-Chem., vol. 8, 1927, pp. 307–309; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 108–114; Chem. Abs., vol. 22, 1928, p. 1458.

These authors repeat the work of Hoffman and Groll (abs. 1453), which purported to show synthesis of hydrocarbons by passing N_2 and steam over activated coke mixed with various metals and metallic oxides as catalyzers. Hoffman and Groll's results were not confirmed.

1000. ———. [Formation of Liquid Hydrocarbons From Acetylene.] Brennstoff-Chem., vol. 10, 1929, pp. 279–282; Chem. Abs., vol. 24, 1930, p. 483.

Experimental method consisted in passing C_2H_2 over silica gel or active C at 600°–700°, the following results being obtained: With pure C_2H_2 at first CH_4 and C were mainly formed, the latter serving as a contact whereby 70% of the C_2H_2 was converted into liquids (heavy oil : light oil = 1 : 1). With distilled C_2H_2, made by decomposing CH_4 in coke-oven gas, the total conversion was smaller, but the light-oil yield was as high as with pure C_2H_2. Distillation with CO_2 favored light oil formation and increased the life of the contact mass; CO_2 could serve for revivifying the catalyst. With CO_2–C_2H_2 mixtures in an empty tube, 70% of the C_2H_2 was converted into oil; reduced pressure was unfavorable.

1001. ———. [Partial Combustion of Methane at Various Pressures With Particular Consideration of Accompanying Acetylene Formation.] Brennstoff-Chem., vol. 11, 1930, pp. 501–507; Chem. Abs., vol. 25, 1931, p. 796.

By use of CH_4–air, CH_4–O_2 and coal gas–O_2 mixtures in various proportions with various flow-rates, temperatures, and pressures, the decomposition of CH_4 has been determined and is shown in tabulated analyses and graphs. A heated porcelain tube passing the gas-air mixtures is used for the low pressures and a bomb for the high pressures. The arrangement and construction are given in diagrams. The importance of time and temperature is demonstrated. A primary formation of —CH and —OH radicals is followed by a secondary decomposition into CO and H_2, making the prompt removal of the C_2H_2 necessary for recovery. These reactions may be accelerated by large catalytic surfaces. Yields of C_2H_2 as high as 50–60% of the CH_4 used have been obtained over a temperature range of 600°–1,500°. The rest of the CH_4 in burning to CO and H_2O, furnishes the necessary heat of formation for the C_2H_2. The use of diminished pressure does not materially increase C_2H_2 formation but does retard the secondary decomposition. Explosion pressures do not produce greater yields. Oxidation and decomposition reactions of CH_4 are briefly discussed.

1002. ———. [Influence of Pressure Upon Several Conversions of Water Gas.] Brennstoff-Chem., vol. 12, 1931, pp. 365–372; Von den Kohlen, vol. 4, 1931, pp. 9–34; Chim. et ind., vol. 28, 1933, pp. 62–63; Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 368–385; Chem. Abs., vol. 25, 1931, p. 5970; vol. 26, 1932, p. 5195.

Elevated pressures hinder the gasification of carbonaceous material by steam because of the surface layer of inert gases so produced. A secondary formation of hydrocarbons results when this is prevented by using high temperatures or addition of alkali, the H_2 already formed then reacting with C. The higher the partial pressure of H_2, the greater is the hydrocarbon formation. In the catalytic hydrogenation of CO, elevated pressure favors the formation of high-molecular hydrocarbons upon catalyst surfaces, which rapidly lessen catalyst effectiveness. O_2-containing products also are formed in addition to hydrocarbons. Lower pressures require greater contact surfaces for equal conversion to hydrocarbons. Pressure strongly affects the manner and rate of CH_4 decomposition by CO_2 or steam. The equilibrium $CH_4+CO_2\rightleftharpoons 2CO+2H_2$ is displaced completely to the right at 1 atm. pressure at 900° in the presence of a Ni catalyst. At 0.003 atm. and 400° only 50% conversion occurs, while at 0.003 atm. and 300° only 25% occurs. Reaction rate increases proportionally with pressure decrease. Temperature and pressure dependence of the equilibrium have been determined and calculated. A literature review is appended.

1003. ———. [Thermal Conversion of Ethylene and Ethane Into Other Hydrocarbons With Particular Regard to the Formation of Acetylene.] Brennstoff-Chem., vol. 13, 1932, pp. 406–411, 435; Chem. Abs., vol. 27, 1933, p. 2016.

Influence of time, distillation with H_2, CH_4, or N_2, 2-stage treatment for liquid products, and partial combustion with O_2 have been studied at high and low pressures for C_2H_4. Quantitative pure thermal dehydrogenation to C_2H_2 depends upon high temperature, a controlled brief time, low pressure, and distillation with H_2. The dehydrogenation of C_2H_6 proceeds by stages, and yields of either 86% C_2H_2 or 72% C_2H_4 are obtainable by the control of similar factors as with C_2H_4. Includes brief review and bibliography.

1004. ———. [Thermal Decomposition of Methane. Benzine and Acetylene Synthesis.] Brennstoff-Chem., vol. 13, 1932, pp. 381–383; Chem. Abs., vol. 27, 1933, p. 2016.

Conditions of CH_4 concentration, temperature, pressure, time, etc., from experimental and theoretical standpoints have been determined for maximum yields of C_2H_2 or C_6H_6. Effects are shown with curves. Brief review and bibliography.

1005. ———. [Thermal Fission of Benzine and Petroleum With Particular Consideration for the Formation of Acetylene.] Brennstoff-Chem., vol. 13, 1932, pp. 441–445; Chem. Abs., vol. 27, 1933, p. 2016.

By use of apparatus previously described, yields of decomposition products at low and atmospheric pressure at 900°–1,400° have been determined and are shown graphically to conform to theories previously advanced. Bibliography.

1006. ———. [Simultaneous Effect of Carbon Monoxide and Carbon Dioxide During Hydrogenation, With Particular Regard to Benzine Synthesis.] Brennstoff-Chem., vol. 14, 1933, pp. 306–310; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 393–402; British Chem. Abs., 1933, B, p. 849; Chem. Abs., vol. 27, 1933, p. 5937.

In previously described apparatus, experiments with various catalysts, as Ni, Co, and Fe, indicate that the presence of CO in a CO_2–H_2 mixture retards catalytic hydrogenation while the presence of CO_2 in a CO–H_2 mixture exerts no influence on the yields of benzine obtained in the synthesis. While only H_2O is obtained in addition to higher hydrocarbons in the hydrogenation of CO and H_2 at temperatures <200°, at higher temperatures CO_2 and CH_4 are obtained as in the water-gas equilibrium, and at still higher temperatures C and CO_2 are formed.

1007. ———. [Conversion of Carbon Monoxide and Carbon Dioxide Into Methane at High Pressures.] Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 386–389; Chem. Zentralb., 1934, II, p. 1062; Chem. Abs., vol. 29, 1935, p. 6565.

It has been previously shown (abs. 1005) that at high pressures the equilibrium $CH_4+CO_2=2CO+2H_2$ is displaced toward the left by increasing the temperature. The reduction of CO at 700° and 70–80 atm., even without a catalyst, was studied experimentally. A Mo catalyst was most satisfactory of those used. With a Ag catalyst considerable C_2H_6 was produced. Even CO_2 was reduced to CH_4 at 600° and 300 atm. without a catalyst. Magnesite thoroughly treated with H_2 yielded C_2H_6 in addition to CH_4.

1008. ———. [Increasing Yields of Fluid Hydrocarbons by Performing the Benzine Synthesis of Franz Fischer and Hans Tropsch in Steps.] Brennstoff-Chem., vol. 17, 1936, pp. 24–29; Ges. Abhandl. Kenntnis Kohle, vol. 12, 1937, pp. 382–393; Chem. Abs., vol. 30, 1936, p. 5764.

Results of laboratory and semi-industrial tests of stepwise synthesis without increasing the amount of catalyst/unit volume of the gases used are described. In the first stage, the 1:2 mixture of CO:H_2 is treated at a temperature so low that the conversion is incomplete, but a good degree of liquefaction of the gases is effected. After a more or less complete extraction of the reaction products the residual CO : H_2 mixture is subjected to a second and possibly a third synthesis. Some of the possibilities of the method are discussed. The semi-industrial trials were made with a Co–Cu–Th precipitated catalyst unsuitable for maximum yield owing to its tendency to form CH_4. The largest apparatus used 10 kg. of Co and 10 m.³ of mixed gas/hr. It is concluded that such a stepwise synthesis increases the yield of liquid hydrocarbons by 10–20%. The durability of the catalyst is increased by arranging that the gas flow (allowing for contraction) is the same/unit weight of catalyst in all stages. Using equally active catalyst in all stages, the yield is highest if the temperature in the 1st stage is lower than in the 2d; by this means 76% of the CO is converted to liquid hydrocarbons. The intermediate removal of products is an essential feature of the method. By 3-stage working, up to 141 gm. of gasoline plus oil can be obtained/m.³ of mixed gas, plus another 10 gm. for the gas oil and the synthetic wax. These figures relate to a gas with 29.5% CO and 60% H_2 for which the theoretical maximum yield is 185 gm. By using higher quality gases, yields exceeding 150 gm./m.³ could be obtained.

1009. ———. [Factors in the Synthesis of Kogasin and Paraffin in Water Phase.] Brennstoff-Chem., vol. 20, No. 13, 1939, p. 247; Refiner and Nat. Gasoline Mfr., vol. 19, 1940, pp. 479–481; Chem. Abs., vol. 35, 1941, p. 1599.

CO and H_2 reacted in the presence of Ni, Co, Fe, and Ru catalysts suspended in water or aqueous solutions. Hydrocarbons, mainly solid, were obtained but only when using Co and Ru. The disappearance of gas, indicating the yield, varied from 50 to 80%. The results were not seriously affected by the presence of 3 *N* solutions of H_3PO_4, HCOOH, CH_3COOH, or $(COOH)_2$. The experiments were performed at 170°–200°.

1010. ———. [Synthesis of Paraffin From Carbon Monoxide and Hydrogen.] Ber. deut. chem. Gesell., vol. 72B, 1939, pp. 327–330; Chem. Abs., vol. 33, 1939, p. 3995.

In the catalytic hydrogenation of CO with Co, Ni, or Fe catalysts at atmospheric pressure chiefly aliphatic hydrocarbons (benzine synthesis) are formed. The working temperatures with Co and Ni are 180°–200° and with Fe 230°–250°. With catalysts that are less favorable to the hydrogenation process, such as ZnO, Cr_2O_3, Mn_2O_3, reaction occurs only at higher temperatures (usually above 300°) and pressures (above 100 atm.), and O-containing compounds are formed, especially MeOH or synthol. Aside from the nature of the catalyst, the temperature and pressure have a decisive influence on the course of the process. With a Co catalyst a slightly increased pressure produces a remarkable change. At 5–20 atm., solid paraffin is the chief product, and the yields of solid + liquid hydrocarbons and the life of the catalyst attain a maximum. Any appreciable increase of pressure above these limits results in a rapid decrease in life of the catalyst. At 50–100 atm. or higher O-containing compounds in increasing amounts with increasing pressures are formed, along with the paraffin hydrocarbons, and volatilization of the catalysts as Co carbonyl begins. The use of Ni is restricted to pressures near atmospheric, for at slight overpressures the activity centers are broken down with formation of Ni carbonyl. The new process, which gives solid paraffin as the chief product, is called the medium-pressure synthesis. With a Co–ThO_2 kieselguhr catalyst (1 : 0.18 : 1) (abs. 984), the following yields were obtained at overpressures of 0, 1.5, 5, 15, 50, and 150 atm., respectively. The yields are expressed in gm./m.³ of so-called ideal gas (inert-free CO–H_2 mixture (1 : 2) at 0° and 700 mm.) employed, not that consumed, and represent the average yields during a 4-week run without renewal of the catalyst: Total solid and liquid hydrocarbons, 117, 131, 150, 145, 138, 104; oil-free paraffin, 10, 15, 60, 70, 54, 27; oil boiling above 200°, 38, 43, 51, 36, 37, 34; benzine boiling below 200°, 69, 73, 39, 39, 47, 43; gaseous hydrocarbons including gasol, 38, 50, 33, 33, 21, 31. The effect of pressure on the life of the catalyst is especially characteristic. At atmospheric pressure the yield of total hydrocarbons fell from 120–130 gm. initially to 100 gm. within the 4-week period; at 1.5 atm. overpressure the yields were better; at 5 and 15 atm. overpressures, even after ½ yr. without regeneration of the catalyst, the yields were still 100–110 gm.; at 50 atm. overpressure they again fell more rapidly; at 150 atm. overpressure the activity of the catalyst decreased with extraordinary rapidity, and in the 2d week the yields fell below 100 gm. The solid paraffin separates in a high degree of purity. The oil-containing product softens at about 60° and melts clear at 90°–100°; after being freed from oil, it begins to melt about 80° and the last solid particle disappears at 100°–115°. By stepwise extraction at the boiling point with different high-boiling solvents, fractions melting up to about 130° can be isolated. The portion boiling above 300° of the total products obtained at 50–20 atm. overpressure contained 85.1–85.2% C and 14.7–14.9% H. The crude liquid hydrocarbons are water-clear and are distributed uniformly through the boiling point range 30°–300°. They are aliphatic and contain only a small amount of unsaturated compounds. The total liquid products contained 84.6–84.8% C and 15.2–15.4% H.

1011. ———. [Synthesis of Paraffin From Carbon Monoxide and Hydrogen Upon Cobalt Catalysts, Medium-Pressure Synthesis.] Brennstoff-Chem., vol. 20, 1939, pp. 41–48; Chem. Abs., vol. 33, 1939, p. 9605.

Laboratory- and semitechnical-scale apparatus is shown schematically and described. The influence of various factors upon the process has been determined. The 1:2 CO–H_2 mixture passed over Co–Th catalyst precipitated on kieselguhr at 185°–190° at the rate of 1 l./hr./gm. Co at pressures to 150 atm. gave maximum yields of solid and liquid hydrocarbons at 5 and 15 atm. in test runs over 4 weeks. White solid products were obtained up to 50 atm.; at 150 atm. O-compounds were found together with Co carbonyl. Maximum paraffin formed at 15 atm. in 70 gm./m.³ yield; oil boiling above 200° increased to a maximum at 5 atm.; maximum gasoline boiling to 200° was obtained at 1.5 atm. Catalyst stability has been determined; its comparatively longer life at 5–15 atm. is outstanding. Reaction temperature is controlled to give maximum conversion and increases up to 190°–195° at 5–15 atm. after 6 months. Increasing pressure to increase throughput reduces conversion. Repeated passage increases conversion. A catalyst containing Cu gives poorer conversion as does the substitution of U for Th. Alkalinization increased yields only at atmospheric pressure. Experiments using 18, 6, 2, and 0% Th show that (1) paraffin is formed in lower yield without Th, (2) the reaction temperatures increase rapidly with lower Th content, and (3) gaseous products increase at the cost of the solid and liquid. Co–Ni upon alloy skeleton improves yields at higher pressures, but these are lower than those with the precipitated catalysts and decrease with time more rapidly. Almost entirely liquid yields are formed and Ni carbonyl is found beginning at 170° when precipitated Ni is used at medium pressures. Under optimum conditions, 50% of the reaction products are paraffins that, freed of oil, melt at 80°–115°. By extraction, fractions melting at 130° may be obtained from them. Fractions boiling 300°–450° indicate products $C_{17}H_{36}$ to $C_{26}H_{54}$. The use of medium pressure increases the fraction boiling above 300°; at 5–20 atm. 13–25% boils above 450°. Of the 30°–300° fraction, half may be considered gasoline and half as diesel oil. Products are water-clear and contain less unsaturated compounds than the usual pressure-synthesis products, these decreasing with increasing molecular weight. Uses possible because of the high melting point of the paraffin are discussed.

1012. Fischer, F., and Priziza, O. [Electrolytic Reduction of Carbon Oxides Dissolved Under Pressure.] Ber. deut. chem. Gesell., vol. 47, 1914, pp. 256–260; Chem. Abs., vol. 8, 1914, p. 1249.

Experiments were conducted in a steel bomb. CO_2 is reduced quantitatively to HCOOH even with high current densities. No evidence of products other than HCOOH was obtained. Attempts to reduce CO in alkaline, acid, and neutral electrolytes using cathodes of Ni, Fe, Cu, Hg, Pt, Ir, and Zn were without result. With Pb electrodes, small current density, preferably an electrolyte of K_2SO_4, and $(NH_4)_2SO_4$, minimal amounts of MeOH were obtained. No CH_4 could be detected.

1013. Fischer, F., and Tropsch, H. [Direct Combination of Carbon Monoxide With Alcohols.] Ges. Abhandl. Kenntnis Kohle, vol. 6, 1921, pp. 382–390; Chem. Abs., vol. 18, 1924, p. 3170.

CO combines with MeOH and EtOH under pressure to form small quantities of formic esters. The reaction is catalyzed by the addition of HCO_2Na on account of the production of free alkali by the interaction of the alcohol and the salt to form the ester. The ester yields are improved by careful drying of the alcohol and formate. The best yield (7.73 gm. of ester/100 gm. of MeOH) was obtained by heating 100 cc. of the alcohol with 10 gm. of HCO_2K and CO under 60 atm. at 180° for 3 hr. in a Cu-lined autoclave, and the yield was only slightly decreased by reduction of the proportion of HCO_2K to 2.5 gm. HCO_2Na also promotes the decomposition of HCO_2Me, so that the addition of CO to alcohols must be regarded as a reversible reaction.

1014. ———. [Preparation of Synthetic Oil Mixtures (Synthol) From Carbon Monoxide and Hydrogen. I.] Brennstoff-Chem., vol. 4, 1923, pp. 276–285; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 475–494; Chem. Abs., vol. 18, 1924, p. 459.

Water gas was freed as completely as possible from S compounds and then treated at a temperature of 400°–450° and at 150 atm. pressure in the presence of Fe and K_2CO_3. An oil and a water layer were formed in which the following products were identified. The acids comprised 10% of the mixture HCO_2H; AcOH, propionic, isobutyric, and higher acids to C_8 were identified. 40% water-soluble and partly soluble alcohols, aldehydes, and ketones were found, such as MeOH, EtOH, PrOH, Me_2CO. and MeEtCO. 48% of the oil was volatile with steam and gave such products as EtCHO, Me_2CHCHO. Et_2CO, MePrCO, higher alcohols to C_8, and hydrocarbons. 2% of the oil is nonvolatile with steam. The oil, synthol, which boils 80°–200° is suitable for motor fuel. By heating synthol for 1 hr. at 450° under pressure a mixture of hydrocarbons was obtained that boiled 50°–300°. The hydrocarbons present were saturated. Naphthalene was one of the products identified.

1015. ———. [Preparation of Synthetic Oil (Synthol) From Carbon Monoxide and Hydrogen. II.] Brennstoff-Chem., vol. 5, 1924, pp. 201–208, 217–227; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1927, pp. 495–533; Chem. Abs., vol. 18, 1924, p. 3705.

Theory of the synthesis of hydrocarbons from water gas under pressure in the presence of Fe and alkalies was discussed previously (abs. 1014). Apparatus is described for the preparation and complete desulfurization of water gas, which is recirculated in a special autoclave containing contact materials for the catalytic production of synthol. Various contact materials are tested, and conditions most favorable to the reactions desired are determined. The following conclusions were reached: (1) For synthol formation the contact material must consist of an H-carrying metal and an alkali; Fe is the best metal, better than Co or Ni, and RbOH or Rb_2CO_3 are the best base. (2) The metal should be in the form of chips, not finely divided. (3) Enough alkali should be used to convert the Fe surface into ferrite; an excess is harmful. (4) For a given amount of contact mass, there is an optimum gas velocity; the optimum temperature is 410° for Fe but higher for Ni. (5) The relative amounts of oily and watery products vary somewhat, even for the same contact material and apparently unchanged experimental conditions; watery products vary most, particularly as regards their alcoholic and ketone content. (6) The Fe catalyst will retain its full activity for a week but gradually becomes reduced to powder; finely divided Fe favors C precipitation from CO, but this is greatly hindered by the alkali. (7) Varying the pressure 70–150 atm. does not affect yields. (8) The richer the gas used is in H_2 the higher the yield of watery products, but the oil obtained is of lower boiling point than that formed when the CO concentration is high; it also contains less hydrocarbons. (9) By a single passage of the gas through the catalyst the yields are low, but by recirculation 27% of the heating value in the gas can be recovered in oil and alcohol formed. Mixtures of CO_2 and H_2 can be used, but they require longer contact than CO and H_2. CH_4 with CO or CO_2 will not yield synthol.

1016. ———. [Reduction of Carbon Monoxide to Methane in the Presence of Iron and Under Pressure.] Brennstoff-Chem., vol. 4, 1923, pp. 193–197; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 463–473; Chem. Abs., vol. 18, 1924, p. 349.

Previous investigators have carried out the reduction of CO to CH_4, using finely divided Ni and Co as a catalyst at 380° in the presence of Fe at 500°–600°. This work was undertaken to study the reduction of CO in contact with Fe under pressure. The apparatus consisted of a heavy iron tube 90 cm. in length by 2.1 cm. inside diameter. The tube was electrically heated. The contact took place over a length of 30 cm. The reduction was studied at 2–100 atm. pressure and at 400°–430°. The gas used consisted essentially of CO and H_2. At 2 atm. pressure only small amounts of CH_4 were formed. At pressures of 45–55 atm. the highest percentage of CH_4 was formed. The reaction may be considered to take place as follows: $CO+3H_2=CH_4+H_2O$. The H_2O formed then reacts with CO—$CO+H_2O=CO_2+H_2$.

1017. ———. [Synthesis of Higher Members of the Aliphatic Series From Carbon Monoxide.] Ber. deut. chem. Gesell., vol. 56B, 1923, pp. 2428–2443; Chem. Abs., vol. 18, 1924, p. 1379.

Having found that formates could be made from CO and bases and that these formates could be converted by thermal decomposition into liquids like MeOH, Me_2CO, etc. (abs. 1013), Fischer and Tropsch, in an effort to obtain liquid fuels suitable for motors, directly in 1 operation, studied the action on water gas of various bases and salts, which under pressure with CO gave formates, spread on a number of carriers, but only when metals, such as Fe shavings, were used as the carrier were they successful. The bases or the metals alone, German Patents 293,787, 295,208 and 295,202, will not do. The water gas, freed as completely as possible of S compounds, was passed under 150 atm. into the contact chamber, containing, for example, K_2CO_3 on Fe shavings, at 400°–450°, and the product was collected under pressure in a cold receiver. This product generally separated into 2 layers, 1 vol. oil and 2 vol. of an aqueous solution, 20% of which consisted of aliphatic alcohols, aldehydes, ketones, and free fatty acids. Of the oil, 41% boiled below 100°, 73% below 150°, 83% below 180°, and 88% below 200°; 1,450 gm. of the crude product, shaken with 5 *N* NaOH, and washed with H_2O, which dissolved about 10% of nonacid constituents, which on fractional distillaton again gave a distillate only partly miscible with H_2O, yielded 943 gm. oil volatile with steam and 41.6 gm. residue; of the volatile portion, 40, 63, 77, 87, 92 and 96% boiled below 100°, 125°, 150°, 175°, 200° and 225°, respectively. Among the acids in the aqueous and oily layers were identified HCO_2H (by reduction of $HgCl_2$), AcOH (anilide), $EtCO_2H$ (basic Pb salt), and Me_2CHCO_2H (conversion into $Me_2C(OH)CO_2H$); the equivalent weights of the higher fractions indicated the presence of acids up to $C_8H_{16}O_2$. The fraction of volatile oil boiling below 100° contained 7.2% aldehyde (calculated as PrCHO) and the fraction boiling above 100°, 25.9%; in the former were identified, by conversion into the acids, EtCHO, PrCHO, and Me_2CHCHO; no HCHO could be detected. Me_2CO, MeCOEt, Et_2CO, and MeCOPr were isolated, the first as the oxime and semicarbazone, the others as the *p*-nitrophenylhydrazones. MeOH was identified through its oxalate, EtOH through its acetate, and PrOH through its *p*-nitrobenzoate; the Ac number of the oil indicated the presence of about 50% alcohols, calculated as $C_6H_{11}OH$; its saponification value indicated a 4% content of ester, as AcOEt. After treatment with $NaHSO_3$, which dissolved 25%, and repeated distillation from Na, the oil yielded 2.5% hydrocarbons $C_{10}H_8$, still containing 0.22% O. Below are the % yields of products thus far identified: Acids, 10 (HCO_2H 0.1, AcOH 2.3, $EtCO_2H$ 2.1, Me_2CHCO_2H 1.0, higher acids 4.5); H_2O-soluble alcohols; aldehydes and ketones, 29 (MeOH 1.5, EtOH 14.5, Me_2CO 5.2); oil partly miscible with H_2O, 11; oil volatile with steam 48% (higher alcohols up to C_9 15.0, esters 2.0, hydrocarbons 1.3); oil not volatile with steam, 2%. The HO-soluble product is designated pyrosynthol, the volatile oil, synthol (=synthetic oil). The latter is converted by heating under pressure into synthin (=synthetic benzine); 25 gm. heated in a 250 cc. autoclave filled with N_2 for 1 hr. at 420° gave 2,250 cc. gas (14.5% CO_2, 22.7% hydrocarbons absorbed by fuming H_2SO_4, 0.7% O_2, 14.6% CO, 9.6% H_2, 21.8% CH_4 hydrocarbons, 16.1% N_2), 17.5 cc. of the dark red-brown oil and 3.5 cc. of an aqueous layer. Of the oil, 4, 10, 17, 22, 35, 48, 57, 65, 74, 78, and 84% boiling below 50°, 75°, 100°, 125°, 150°, 175°, 200°, 225°, 275°, and 300°, respectively. The fraction boiling below 100° had a benzinelike odor and only slightly colored concentrated H_2SO_4. Of the fraction boiling above 100°, 50% dissolved in concentrated H_2SO_4. The insoluble portion, washed with H_2O and Na_2CO_3 and distilled with steam, had a pronounced petroleum odor and 24, 44, 27, and 5% boiled at 120°–150°, 150°–200°, 200°–270°, and above 270°, respectively; it consisted of hydrocarbons ranging from C 84.48, H 15.14%, d_4^{20} 0.762 for the 75°–100° fraction to C 88.43, H 12.05%, d_4^{20} 0.874 for the 200°–270° fraction. The H_2SO_4 solution on dilution with H_2O gave an oil 33. 54, and 13% of which boiled at 100°–175°, 175°–235°, and above 235°, respectively; the 175°–235° fraction contained 79.05% C and 11.20% H. Outside of Fe, only those of the nonnoble metals that are known to be H carriers, Ni, Co, and possibly Mn, will effect the above reaction; a base or salt of a base with a weak acid is also essential, and apparently the oil formation proceeds more satisfactorily the stronger the base. The various possible mechanisms of the reaction are briefly discussed.

1018. ———. [Direct Synthesis of Petroleum Hydrocarbons at Ordinary Pressure. I, II.] Ber. deut. chem. Gesell., vol. 59B, 1926, pp. 830–831, 832–836; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 190–206; Chem. Abs., vol. 20, 1926, p. 2814.

With metals of the 8th group as catalysts, the catalytic hydrogenation of CO at ordinary pressure yields not CH_4 alone but a mixture of CH_4 with its homologs. By following the reaction quantitatively, it was found that the first C derived from the CO is taken up by the catalyst, evidently with carbide formation, and from this carbide, present in the finest state of subdivision, the H_2 regenerates the metal and removes the C as hydrocarbons. The carbides are apparently not the normal, low-C compounds stable at high temperatures but compounds rich in C and stable only at relatively low temperatures, and as a result, the C is removed from them not as CH_4 but as polymembered homologs of CH_4. That in this process the hydrocarbons are not formed through HCHO or MeOH as in the high-pressure catalysis is confirmed by the fact that only hydrocarbons and never O-containing organic compounds are formed. At temperatures such as are used in the high-pressure method, only CH_4 is formed. Finely divided Co is an efficient catalyst, Fe is slower, and Ni is quite weak in the ability to produce hydrocarbons other than CH_4. Better than the metals alone are mixtures of them (1–3 parts) with other substances (oxides of Cr, Zn, Be, the rare-earth metals, U, Si, Al, Mg, and Mn, active charcoal and amorphous C in other forms); faintly alkalinizing the Fe metal increases its catalytic activity. The absence of toxic S compounds must be insured. Commercial mixtures of CO and H_2 (especially water gas) may be used, S compounds being first removed by catalytic conversion into H_2S under conditions that will not change the composition of the gas as regards its other components; such a method of purification will be described elsewhere. With all the gases used (water gas, mixtures poorer and richer in CO, moist CO, etc.), benzine was obtained if they had been sufficiently purified. It is especially important to keep the temperature as low as possible (around 300° with Fe, 270° with Co, and 160° with Ni). The higher the velocity of flow the more can the formation of CH_4 be suppressed but the poorer, of course, is the utilization of the gas mixture. A part of the reaction product condenses in liquid form as soon as the reaction mixture cools, and the rest, remaining in the gas in vapor form, is recovered by the usual methods. The condensed products are, depending on conditions, light oils like illuminating oil but also may contain higher boiling oils and deposit solid paraffin. The benzines are H_2O clear with a pleasant odor, resembling Pennsylvania benzine, and contain only a few % of substances reacting with concentrated H_2SO_4 and do not change at all on standing. The only other products besides hydrocarbons are CO_2 and H_2O. In an experiment with an Fe–Co catalyst, about 100 gm. of liquid and easily liquefiable products were obtained per m.³ of water gas.

1019. ———. [Reduction and Hydrogenation of Carbon Monoxide.] Brennstoff-Chem., vol. 7, 1926, pp. 299–300; Ges. Abhandl. Kenntnis Kohle, vol. 8, 1929, pp. 207–208; Chem. Abs., vol. 21, 1927, p. 642.

Fischer and Tropsch comment on the findings of Elvins and Nash (abs. 817 and 818). They disagree with their suggestion that at atmospheric pressure hydrocarbons result through preliminary formation of synthol and subsequent dehydration by catalysis. They maintain that formation of hydrocarbons results from the intermediate formation and decomposition of unstable carbides.

1020. ———. [Some Properties of the Synthetic Petroleum Hydrocarbons Prepared From Carbon Monoxide at Ordinary Pressure.] Ber. deut. chem. Gesell., vol. 59B, 1926, pp. 923–925; Chem. Abs., vol. 20, 1926, p. 2815.

The gas-oil fraction contains C_2H_6, C_3H_8, and C_4H_{10}; the corresponding olefins are present in only very subordinate amounts. The benzine, isolated by adsorption with active charcoal and distillation with steam, is H_2O-clear, stable to light, has a pleasant odor, does not turn yellow or resinify on standing for months. d_4^{15} 0.6718, upper heat value 11,360 cal. per gm., ignition temperature in O_2 335°, b. p. 2.4 vol. % up to 40°, 96.4% up to 180°, d_4^{20} from 0.6367 for the 20°–55° fraction to 0.7264 for the 120°–180° fraction. C and H_2 for the same fractions 84.23, 16.50, and 83.35, 14.96%, respectively. upper heat value of the 75°–120° fraction 11,495 cal. per gm. The petroleum fraction, d_4^{20} 0.7804, b. p. 4.4 vol. % 170°–180°, 83.2% up to 330°, d_4^{20}, C and H_2 for the 170°–270° fraction (58.4 wt. % of the total) 0.7646, 85.04%, 14.94% (heat value 11,225 cal. per gm.), for the 270°–330° fraction (24.1%) 0.7972, 85.36, 14.41. The paraffin fraction freed from adhering paraffin oil with Me_2CO is colorless, odorless, solidifies at 61°, and has a C content of 84.57% and H of 14.57%. The synthetics differ from the natural products in that they require no refining and are wholly free of S compounds.

1021. ———. [Synthesis of Petroleum at Atmospheric Pressures From Gasification Products of Coal.] Brennstoff-Chem., vol. 7, 1926, pp. 97–104; Nat. Petrol. News, vol. 18, No. 41, 1926, pp. 95–96, 99; No. 42, pp. 80C, 80D, 80E, 80F, 80H; Chem. Abs., vol. 20, 1926, p. 2065.

S-free mixture of CO and H_2 (water gas) is passed over finely divided metals of the 8th group, alone or mixed with metallic oxides, such as those of Zn and Cr, at a temperature approximately 270° and atm. pressure. At higher temperatures, CO is reduced to CH_4, but by selecting the catalyst mixture and keeping the temperature down, only saturated higher homologs of CH_4 are formed. These vary in molecular complexity from C_2H_6 to solid paraffin. O appears in the reaction products almost wholly as CO_2 and H_2O. The