

241. ———. [Hydrogenation of Coal and Heavy Oils for Production of Airplane Fuels.] *Génie civil*, vol. 114, 1939, pp. 214-216, 234-237.

Recent progress is shown and statistical data are given on the production of synthetic fuels in France. The economic organization of a synthetic-fuel industry is outlined.

242. ———. [Synthetic and Substitute Fuels for Internal-Combustion Motors.] *Chim. et ind.*, vol. 44, 1940, pp. 463-470; *Chem. Zentralbl.*, 1941, I, p. 1629; *Chem. Abs.*, vol. 37, 1943, p. 2907.

Present-day accomplishments and trends in the production of synthetic-hydrocarbon fuels—hydrogenation, catalytic cracking, polymerization, isomerization, alkylation, Fischer process, and addition of PbEt<sub>2</sub>—are outlined in a lecture.

243. ———. [The Complex Coal-Chemistry-Petroleum.] *Chim. et ind.*, vol. 45, 1941, pp. 551-554; *Chem. Abs.*, vol. 38, 1942, p. 3025.

At the *Établissements Kuhlmann* in Pas-de-Calais gases containing CH<sub>4</sub> are heated with O<sub>2</sub> and steam in the presence of active Ni on a refractory support (the catalytic activity lasts for more than 1 yr.) according to the equations CH<sub>4</sub>+0.5 O<sub>2</sub>=CO+2H<sub>2</sub> and CH<sub>4</sub>+H<sub>2</sub>O=CO+3H<sub>2</sub>. Gives other references to coal-hydrogenation processes.

244. ———. [Production of Methanol and Its Derivatives. Formaldehyde, Hexamethylenetetramine, Resins, etc.] *Chim. et ind.*, vol. 45, Special No. 42-43, 1941; *Chem. Zentralbl.*, 1942, I, p. 418; *Chem. Abs.*, vol. 37, 1943, p. 2715.

245. ———. Program for Synthetic and Substitute Fuels. *Jour. Soc. Auto. Eng.*, vol. 15, 1942, p. 265.

Discusses use of peat for fuel in France. Includes some remarks concerning the production and utilization of alcohol and synthetic gasoline.

246. ———. [Some Aspects of the Fuel Industry. Conversion of Methane into Carbon Monoxide and Hydrogen by the Action of Steam in Presence of Catalysts.] *Chim. et ind.*, vol. 52, 1944, pp. 153-154; *Chem. Abs.*, vol. 40, 1946, p. 2958.

Brief description of method and precautions required.

247. ———. [Synthetic and Substitute Lubricants.] *Chim. et ind.*, vol. 53, 1945, pp. 160-166; *Chem. Abs.*, vol. 42, 1948, p. 6096.

To replace imported petroleum products, lubricants can be obtained from anthracene oil, rosin oil, shale oil, low-temperature tar, and coal (by hydrogenation or by Fischer-Tropsch synthesis). The development of vegetable-oil production in North Africa will provide open-chain material for Friedel-Crafts syntheses on a C<sub>6</sub>H<sub>6</sub> nucleus, and the chemical or electrical polymerization of C<sub>6</sub>H<sub>6</sub> can also yield lubricants.

248. BERTHELOT, C., AND HOR, M. Carburants de synthèse et de remplacement. H. Dunod, Paris, 1936, 350 pp.; *Chem. Abs.*, vol. 31, 1937, p. 241.

249. ———. Technique et économie nouvelles des carburants de synthèse. H. Dunod, Paris, 369 pp.; *Chem. Abs.*, vol. 32, 1938, p. 4312.

Reviewed in *Bull. assoc. chim.*, vol. 55, 1938, p. 268; *Coal Carbonization*, vol. 4, 1938, p. 50.

250. BERTHELOT, D., AND GAUDECHON, H. [Photochemical Synthesis of Carbohydrates From Carbon Dioxide and Water.] *Compt. rend.*, vol. 150, 1910, pp. 1690-1693; *Jour. Soc. Chem. Ind. (London)*, vol. 29, 1910, p. 904.

Oxides of C and water vapor have been made to react with each other by means of the light of the Hg vapor lamp. CO and O<sub>2</sub> produce a small amount of CO<sub>2</sub>, while the latter gas yields CO when exposed to the rays in the presence of P. CO<sub>2</sub> and H<sub>2</sub> give H<sub>2</sub>O

and HCHO. HCHO can be made directly from H<sub>2</sub> and CO.

251. BERTHELOT, M. [Chemical Effects of the Silent Electric Discharge.] *Compt. rend.*, vol. 126, 1898, pp. 561-567, 567-575, 609-616, 616-627; *Jour. Chem. Soc.*, vol. 1, 1898, pp. 393-396.

Various mixtures of CO and H<sub>2</sub> were subjected to the action of the silent discharge. Some carbohydrates of the general formula (CH<sub>2</sub>O)<sub>n</sub> were obtained.

252. ———. [Chemical Equilibrium Between Hydrogen and the Oxides of Carbon.] *Ann. chim. phys.*, ser. 7, vol. 14, 1898, pp. 170-176; *Jour. Chem. Soc.*, vol. 2, 1899, p. 286.

CO<sub>2</sub> when heated at high temperatures is partly dissociated into CO and O<sub>2</sub>. In the presence of C or H<sub>2</sub>, the O<sub>2</sub> thus liberated is employed in oxidizing this element, and further dissociation of CO<sub>2</sub> must take place to preserve the equilibrium. When a mixture of CO<sub>2</sub> and H<sub>2</sub> is raised to a high temperature, equilibrium is established, not between the binary systems (CO<sub>2</sub>+H<sub>2</sub>) and (CO+H<sub>2</sub>O) but between the more complicated system [(n-a) CO<sub>2</sub>+a (CO+O)] resulting from the partial dissociation of CO<sub>2</sub> and that produced by the partial dissociation of steam [(m-b) H<sub>2</sub>O+b (H<sub>2</sub>+O)] and a further complication results from the dissociation of CO which reacts as follows:  $p\text{CO} = (p-2)\text{CO} + \text{C}$ . This explanation is based on the observed behavior of these compounds at high temperatures, each of them dissociating in the manner indicated, independent of the presence of the others.

253. ———. [Generation of Hydrocarbons by Metallic Carbides.] *Compt. rend.*, vol. 132, 1901, pp. 281-290; *Jour. Chem. Soc.*, vol. 1, 1901, p. 245.

Mentions or discusses following carbides: Acetylides, Na, Li, Ca, Ag, Al, Mn, Ce, La, Y, and U.

254. ———. [Study of Chemical Reactions.] *Ann. chim. phys.*, vol. 6, 1905, (S), p. 183; *Compt. rend.*, vol. 140, 1905, pp. 905-914; *Jour. Chem. Soc.*, vol. 88, 1905, (2), p. 308A.

Attempt was made to cause the direct synthesis  $\text{C} + 2\text{H}_2 = \text{CH}_4$  by passing H<sub>2</sub> through quartz tubes heated to 1,300°. Results were negative although Bone and Jerdan had effected the direct synthesis at 1,200° over pure-sugar C (abs. 296).

255. BERTHELOT, M. A. L'Industrie des combustibles liquides. Part 2. Les Carburants de synthèse. Gauthier-Villars & Cie, Paris, 42 pp.; *Chem. Abs.*, vol. 30, 1936, p. 3971.

BEVER, M. B. See abs. 2562.

256. BHATIA, G. L. Synthetic Petroleum. 1950, XV, 92 pp.; *Nature (review)*, vol. 166, 1950, p. 624.

Object of this booklet about synthetic gasoline is to arouse the interest of laymen, manufacturers, chemists and engineers, and the Government of India to the vital importance of building up a key industry on national lines comparable with what has already been done in America, Britain, Germany, and Japan.

256a. BHATTACHARYA, S. K., AND RAO, B. C. S. Oxo Process. I. Synthesis of Propionaldehyde from Ethylene, Carbon Monoxide and Hydrogen in the Gas Phase in the Presence of Cobalt Catalysts at High Pressures. *Jour. Sci. Ind. Research (India)*, vol. 11 B, 1952, pp. 80-81; *British Abs.*, 1952, B II, p. 794.

In preparing propionaldehyde by the Oxo process, the optimum conditions are: A gas mixture of C<sub>2</sub>H<sub>4</sub>, CO, and H<sub>2</sub> (1:1:1), 150°, 150 atm. (3 hr.), and a catalyst containing 20% of Co (prepared by precipitating from nitrate solution with K<sub>2</sub>CO<sub>3</sub>) on kieselguhr.

BILJOVIC, P. See abs. 2433.

257. BILLIG, R. Studies on Solid Paraffin Hydrocarbons Which Originate in Gasoline Synthesis Accord-

ing to Fischer-Tropsch, and on Conversion of Produced Cracking Process Distillates Rich in Olefins Into Lubricating Oils. FIAT Reel C268, 1939, frames 4687-4693; PB 73,606.

See abs. 1818, 1819.

258. BINDER, G. G., AND WHITE, R. R. Synthesis of Methane From Carbon Dioxide and Hydrogen. *Chem. Eng. Progress.*, vol. 46, No. 11, 1950, pp. 563-574.

Rate of formation of CH<sub>4</sub> from CO<sub>2</sub> and H<sub>2</sub> was measured by passing feed gas ranging in composition from 80% H<sub>2</sub> and 20% CO<sub>2</sub> to 30% H<sub>2</sub> and 70% CO<sub>2</sub> over a reduced Ni catalyst in a continuous apparatus. Several runs were made in which the feed gas contained CH<sub>4</sub>. The space time was varied from 0 to 8 x 10<sup>-3</sup> hr. The temperature range was 500°-750° F., and the pressure was maintained at 1 atm. in all runs. Average rates of CH<sub>4</sub> formation, obtained by differentiation of the data, vary from 0-5.60 lb. per mole (lb. catalyst). Rate of reaction can be correlated by a mechanism that assumes that the major resistance to the overall process is offered by the re-adsorption of an adsorbed CO<sub>2</sub> molecule with at least 2 action of an adsorbed H<sub>2</sub> molecule. Presents two equations for adsorbed H<sub>2</sub> molecules. Presents two equations for the rate of CH<sub>4</sub> formation resulting from the extremes of the range of correlating mechanisms.

259. BIRCH, S. F., WITHERS, J. G., NARRACOTT, E. S., AND HABESHAW, J. Miscellaneous Information on Fuels, Detergents, and Lubricants. BIOS Final Rept. 1646, 1946, 160 pp., PB 91,685.

Gives general notes on the Michael hot-gas recycle and the foam processes, the Ruhrechemie method of olefin analysis, description with diagram of a Kaiser Wilhelm Institute capillary flowmeter for measuring gas flows at high pressures, and some discussion of Rheinpreussen Fe catalysts of composition 100% Fe, 1.7% Cu, 0.1-2% K<sub>2</sub>CO<sub>3</sub>, and 50-100% kieselguhr. The Oxo reaction is also discussed, and a translation of a report by Dr. Nienburg on its development is given. Also gives considerable space to lubricants and lubricating-oil additives. An appendix offers a report of 30 pp. by Dr. Sasse on the explosive limits and flame velocities in hydrocarbon-oxygen mixtures.

260. BIRK, E., AND NITZSCHMANN, R. [High-Pressure Synthesis of Dimethyl Ether and Its Theoretical Foundations.] *Metallbörse*, vol. 19, 1929, p. 2807; *Rept.*, vol. 20, 1930, pp. 1295-1296, 1351, 1407; *Chem. Abs.*, vol. 24, 1930, pp. 2106, 5719.

Critical review of the literature and calculation of equilibrium conditions for the formation of dimethyl ether from MeOH. A tabulation of the volume relations of the reaction gases for 50% and 100% conversions to dimethyl ether. Discusses the formation of di- and tri-ethyl ether along with the synthesis of MeOH from water gas. Expresses water-gas-MeOH equilibrium for pressures of 100-400 atm. and for temperatures 300°-400°. Calculates volume relation of the reaction gases for a direct formation of dimethyl ether combined with the MeOH synthesis. Tabulates calculated values, and lays basis for a MeOH output of 10-50% and a 50-100% conversion of MeOH to dimethyl ether. Another table gives, for the same relations, the amounts of water gas necessary for the production of 1 kg. of dimethyl ether.

261. ———. [Methanol Synthesis and Its Theoretical Basis.] *Metallbörse*, vol. 19, 1929, pp. 1350-1351, 1405-1406, 1462-1464, 1573-1575, 1629-1632, 1742-1744, 1798-1799, 1910-1912; *Chem. Abs.*, vol. 23, 1929, p. 5157.

Outlines development of synthetic processes for the production of MeOH and explains fully fundamental equations for the gas reactions involved; 141 such equations, with deductions from them, curves involved, etc., are given.

262. BISHOP, T. Tonnage Oxygen Plant. Iron and Coal Trades Rev., vol. 156, 1948, pp. 733-739.

Description of the Oxyton plant designed by La Société Anonyme l'Air Liquide of Paris illustrates layout of equipment for producing 100 ton per day of O<sub>2</sub> of 92% purity, using 3 units in parallel and utilizing power at the rate of 340 kw-hr. per ton of O<sub>2</sub> and 0.53 kw-hr. per m.<sup>3</sup> of 100% O<sub>2</sub>.

BLACKBURN, W. H. See abs. 691, 692, 693, 694.

262a. BLANCHARD, A. A., AND GILMONT, P. Preparation of Cobalt Carbonyl, Cobalt Nitrosyl Carbonyl and Cobalt Carbonyl Hydride by the Cyanide Method. *Jour. Am. Chem. Soc.*, vol. 62, 1940, pp. 1192-1193; *Chem. Abs.*, vol. 34, 1940, p. 4354.

An alkaline suspension of a Co salt absorbs CO almost quantitatively to form KCo(CO)<sub>4</sub>, but only in the presence of a carrier such as a small amount of a cyanide. Treatment of KCo(CO)<sub>4</sub> with NO gives Co(NO)(CO)<sub>4</sub>. The addition of an excess of HCl to the reaction mixture gives the volatile HCo(CO)<sub>4</sub>, which condenses at -79° to a solid; it melts at -33° and decomposes above that temperature into (Co(CO))<sub>2</sub> and H<sub>2</sub>.

263. BLAND, W. F. Gasification of Coal May Fore-shadow New Industry Replacing Oil Refineries. *Nat. Petrol. News*, vol. 39, No. 14, 1947, pp. 23-24.

An announcement of the joint plans of Standard Oil Co. of New Jersey and the Pittsburgh Consolidation Coal Co., for gasifying coal and converting it to liquid fuels, high-B. T. u. gas, and chemicals. The plans have only reached the design stage of a \$300,000 demonstration pilot plant to continue the studies and bring the process to a commercial basis. It is expected that the pilot plant will be ready for operation by the end of 1947 and the commercial plant by 1950 or 1951. The pilot plant, as planned, will be devoted primarily to studies of the application of the fluidized-solids technique to coal gasification. About 50 tons of coal/day will be consumed, producing about 2.4 million cu. ft. of gas. Powdered coal in suspension is reacted with O<sub>2</sub> and steam in the generator, and the gas produced is suitable for the synthesis of hydrocarbons by the Fischer-Tropsch reaction. The flexibility of the operation may be used to obtain the maximum yield of domestic fuel gas or for the greatest possible yield of gasoline and other liquid fuels.

264. ———. Processing Coal Into Liquid Products May Be Practicable in a Few Years. *Petrol. Processing*, vol. 2, 1947, pp. 325-327.

Editorial comment on recent developments in coal processing as follows: The Standard Oil Co.-Pittsburgh Consolidation Coal Co. announcement; the report on the coal industry in Fortune magazine; experiments in the underground gasification of coal in Alabama; and the economic picture of coal resources and utilization.

265. ———. Synthesis Gas From Solid Fuels. *Petrol. Processing*, vol. 2, 1947, pp. 731-733.

Brief reviews of the more important papers given at the symposium on Production of Synthesis Gas at the 112th meeting of the Am. Chem. Soc.

266. ———. Oil's Synthetic Fuels. *Nat. Petrol. News*, vol. 40, No. 7, 1948, pp. 22-23; *Petrol. Processing*, vol. 3, 1948, pp. 203-206.

Survey of research and development work done and planned by several members of the oil industry up to the present on the production of synthetic liquid fuels.

267. ———. Oil A-Plenty—But Bureaucrats Press for a Synthetic-Fuel Industry. *Petrol-Processing*, vol. 4, No. 6, 1949, pp. 653-654.

Editorial criticism of the attempt by the Department of the Interior and the Bureau of Mines "to force synthetic fuels upon the country." The argument, sup-

ported by the opinions of oil-industry executives, leads to the conclusion that the time is not ripe for Government intervention in the fuel program. The oil industry itself is capable of supplying all the fuel needed for any and every purpose. So extraordinarily rapid is the progress of technical development, commercial plants erected now for the production of synthetic fuels would be obsolete before they could even be built.

268. BLAND, W. F., AND UHL, W. C. Bureau of Mines Asks Thirty Million Dollars More for Synthetic Liquid Fuels Research. *Petrol. Processing*, vol. 2, 1947, pp. 86-87.

Comments on the bill recently introduced in the Senate by Senator O'Mahoney extending the Bureau of Mines program of research on synthetic liquid fuels. Presents abstracts from the progress report recently made by the Secretary of the Interior and a tabulated summary of actual and estimated expenditures for the years 1945 to 1948, inclusive.

BLASCHCZYK, G. *See abs.* 1498.

269. BLASS, K. [Influence of Raw Materials on the Synthesis of Fatty Acids.] *Fette u. Seifen*, vol. 51, 1944, pp. 221-223; *Chem. Abs.*, vol. 42, 1948, p. 8773. Discusses production of synthetic fatty acids by the paraffin-oxidation process, with refs.

270. BLATCHFORD, J. W. Oxygen Replaces Air in Water-Gas Process. *Chem. Eng. News*, vol. 28, 1950, p. 1022.

Abstract of paper presented at the chemical conference of the Am. Gas Assoc. Operation is described of a 360-ton/day O<sub>2</sub> plant built for the DuPont Co., by Linde Air Products Co., together with several mechanical blue-gas sets. The rate of O<sub>2</sub> feed to the generators in general was low, although in 1 test the flow averaged 2,000 cu. ft./min. for 45 hr. No loss in product quality at this high rate of gasification is reported as compared with the normal rate, which is about 25% lower. At normal operating conditions the units used about 23.7-lb. of coke, 243 cu. ft. of O<sub>2</sub>, and 32.4 lb. of steam to make a million cu. ft. of water gas. The use of O<sub>2</sub> for this process appears to be decidedly advantageous because of the increase in capacity it permits, as well as from the standpoint of fuel consumption and maintenance of equipment. It seems probable that almost any kind of fuel can be used and almost any type of gas maker be modified to use O<sub>2</sub>.

BLUM, P. *See abs.* 215.

271. BLUMENTHAL, L. M. Activated-Carbon Production in Germany During the War. *FIAT Final Rept.* 1181, 1947, 21 pp.; PB 85,143.

General review of German developments in the production and uses of activated C in such fields as gas-mask C, C-depollarizer for dry cells, purification of water, decoloring of boiler condensate, industrial vapor and gas adsorption, and regenerated cellulose fiber containing active C. The production capacity of plants had increased from a total of 990 tons in 1939 to 1,377 tons per month in 1944. A list of trade names is appended. Particular attention was paid to the use of gas-adsorption carbons in the Fischer-Tropsch synthesis. A higher recovery of C<sub>2</sub>H<sub>4</sub> was achieved by increasing the size of adsorbers and by the use of special gas-adsorption carbons, TS and SK identical with type G used in gas masks. SK, an improved supersorbion, 4 mm., 400 gm. per l., was found to be 50-60% more effective than supersorbion T for this application. SK carbon also was found to be very effective in the adsorption of C<sub>2</sub>H<sub>4</sub> and of CH<sub>4</sub>. Purification of gas for the Fischer-Tropsch process can be carried out as follows: H<sub>2</sub>S is removed, then a treatment with supersorbion follows at room temperature to remove gum-forming hydrocarbons, dienes, indenes, and stable cyclic S compounds. The supersorbion is regenerated by the Bayer procedure and liquid-aromatic fuel obtained in this manner. Labile

S compounds such as COS are then eliminated by purifying with alkaline Fe hydroxide at 150°-300°. Continuous use of the Fischer-Tropsch catalyst for 6-7 months is insured by this treatment of the gas, which lowers the S content to less than 0.1 gm. per 100 m.<sup>3</sup>

BLUDOV, A. P. *See abs.* 2772, 2774.

272. BÖNN, W. [Gaseous and Solid-Fuel Substitutes.] *Przeglad gorniczo-hutniczy*, vol. 29, 1937, pp. 353-397; *Chem. Zentralbl.*, 1937, II, p. 4142; *Chem. Abs.*, vol. 33, 1939, p. 6020.

Review of use of motor fuels coming from sources other than petroleum.

273. ———. [Production of Synthetic Benzene From Coal.] *Przeglad Tech.*, vol. 77, 1938, pp. 277-286; *Chem. Abs.*, vol. 33, 1939, p. 9589.

Review.

274. ———. [Progress in the Technique of Liquefaction of Coal.] *Przeglad gorniczo-hutniczy*, vol. 30, 1938, pp. 67-78; *Chem. Zentralbl.*, 1938, II, p. 2873; *Chem. Abs.*, vol. 34, 1940, p. 6041.

Review of the development of hydrogenation, low-temperature carbonization, extraction (method of Pott and Broche), the Japanese hydrogenation process, and the synthesis of hydrocarbons from CO and H<sub>2</sub> by the methods of Fischer-Tropsch, of Robinson-Bindley, and of the I. G. Farbenindustrie A.-G. Considers costs of individual methods.

275. ———. [Synthetic Motor Fuel in Poland and Austria.] *Przemysl Naftowy*, vol. 13, 1938, pp. 311-318; *Chem. Zentralbl.*, 1939, I, p. 864.

Hydrogenation and synthesis motor fuel and their use.

276. ———. [Progress in the Field of Coal Hydrogenation.] *Przeglad gorniczo-hutniczy*, vol. 31, 1939, pp. 112-121. *Chem. Zentralbl.*, 1940, I, p. 811.

Report on the present status of the production of liquid fuels from coal and recent improvements in the hydrogenation and synthesis processes.

BOCCAREDDA, M. *See abs.* 2390.

BOCHAROVA, E. M. *See abs.* 725.

277. BOCHAROVA, E. M., AND DOLGOV, B. N. [Synthesis of Formaldehyde From Water Gas.] *Jour. Gen. Chem.* (U. S. S. R.), vol. 4, 1934, pp. 145-152; *Chem. Abs.*, vol. 28, 1934, p. 5211.

Best results of 0.5-1.2% CH<sub>2</sub>O were obtained with 4MgO.Mn<sub>2</sub>O<sub>3</sub> catalyst at 400° and 150 atm. pressure.

278. ———. [Synthesis of Higher Alcohols From Water Gas Under Pressure. I.] *Compt. rend. acad. sci.*, U. R. S. S., vol. 3, 1934, pp. 115-118 (in English, pp. 118-120); *Chem. Abs.*, vol. 28, 1934, p. 6698.

CO and H<sub>2</sub> react under pressure with alkaliized MeOH catalysts to give a condensate consisting mainly of a mixture of various alcohols (from Me to octyl). Syntheses were carried on in a circulation apparatus with 4 l. capacity at a temperature of 350°-450° and with a falling (220-150 atm.) or constant (220 atm.) pressure and a space velocity of 5,000-6,000. In every case, 300 cc. of the catalyst in the form of shavings was used. The optimum ratio of CO : H<sub>2</sub> was about 1 : 1. Zn aluminates gave unsatisfactory results. The substitution of Na for K completely cuts down the yield of oil. The group of catalysts (4ZnO.PbO, 4ZnO.PbO.Zn(OK)<sub>2</sub>, 4ZnO.PbO.O.2Zn(OK)<sub>2</sub>, and 4ZnO.PbO.O.2Zn(OK)<sub>2</sub>.CaO) gave very low yields for all attainable temperatures. Alkaline-Zn vanadates, 4ZnO.V<sub>2</sub>O<sub>5</sub>.KOH and 8ZnO.V<sub>2</sub>O<sub>5</sub>.KOH, gave the best results. An increase in percentage of Zn lowers the yield. A decrease in V<sub>2</sub>O<sub>5</sub> content from 34.24% to 8.06% lowers the yield of oil from 41 to 17%.

279. BOCHAROVA, E. M., DOLGOV, B. N., AND PETROVA, Y. N. [Synthesis of Higher Alcohols From Water

Gas Under Pressure. II.] *Jour. Chem. Ind.* (U. S. S. R.), vol. 12, 1935, pp. 1249-1255; *British Chem. Abs.*, 1936, B, p. 404; *Chem. Abs.*, vol. 30, 1936, p. 2171.

Apparatus used is the same as that for MeOH synthesis, but the catalyst is more alkaline, and the rate of gas flow is slower, but the temperature is higher (400°-425°) than for MeOH. The pressure is 220 atm. A ratio of H<sub>2</sub> : CO of close to 1 : 1 is best. CO tends to accumulate in recirculated gases. Zn-V catalysts are better than Zn-Al ones, but the best is 8ZnO.AL(OK)<sub>2</sub>.O.V<sub>2</sub>O<sub>5</sub>. The total yield of alcohols is 60% of which 35% is MeOH. The others are EtOH, PrOH, iso-PrOH, BuOH, and iso-BuOH.

280. BOCHAROVA, E. M., DOLGOV, B. N., AND PROKHOROVA, Z. M. [Synthesis of Higher Alcohols From Water Gas Under Pressure. III.] *Khim. Tverdogo Topliva*, vol. 6, 1935, pp. 665-680; *Chem. Zentralbl.*, 1936, II, p. 4254; *Chem. Abs.*, vol. 30, 1936, p. 8147.

Syntheses of higher alcohols were accomplished in the Fischer circulating apparatus of 4.5-l. capacity, at 350°-425°, 220 atm. pressure, with a volumetric velocity of the order 6,800-8,400 (time of contact, 26.5-29 sec.) and a duration of 1 hr. In all cases 300 ml. of catalyst were used. The mixture of CO and H<sub>2</sub> was taken in the proportion 1 : 1, as this was found to be best in previous experiments. (See abs. 278.) The best catalyst was found to be 8ZnO.AL(OK)<sub>2</sub>.O.1-V<sub>2</sub>O<sub>5</sub>, which gives 47% of an oily layer with a yield of 225 ml. of oil/hr./m.<sup>3</sup> of gas. The total content of alcohol higher than MeOH in the condensate was found to be 35%, along with 60% MeOH. Qualitatively the aqueous condensate consists of: MeOH, EtOH, iso-PrOH, and the oily layer of C<sub>2</sub>H<sub>5</sub>OH and a mixture of C<sub>2</sub>H<sub>5</sub>OH, mainly iso-BuOH. 22 refs.

281. BOCHAROVA, E. M., DOLGOV, B. N., PETROVA, Y. N., AND YATSKOVSKAYA, N. S. [Synthesis of Alcohols of High Molecular Weight From Water Gas Under Pressure. IV. Rechecking of the Methods for Analysis of the Condensate.] *Khim. Tverdogo Topliva*, vol. 8, 1937, pp. 533-548; *Chem. Abs.*, vol. 32, 1938, p. 1431.

Existing methods for the analysis of the condensate investigated and rechecked. 26 refs.

282. BOCHAROVA, E. M., DOLGOV, B. N., KAN-KOGAN, K. I., AND PETROVA, Y. N. [Synthesis of Higher Alcohols From Carbon Dioxide and Hydrogen Under Pressure. V.] *Khim. Tverdogo Topliva*, vol. 8, 1937, pp. 1107-1121; *Chem. Abs.*, vol. 32, 1938, p. 4518.

This method was described previously. The synthesis was carried out at 350°-425° at a constant pressure of 220 atm. The previously described catalysts, 8ZnO.AL(OH)<sub>3</sub>.O.1 V<sub>2</sub>O<sub>5</sub>.3KOH and 8ZnO.AL(OH)<sub>3</sub>.O.1 V<sub>2</sub>O<sub>5</sub>.O.1 MoO<sub>3</sub>.3KOH used in the above synthesis yielded water 70%, MeOH 25%, and higher alcohol 5% by weight of the condensate. The best CO<sub>2</sub> : H<sub>2</sub> ratio for the synthesis of higher alcohols than MeOH was 1 : 2.2. The yield of alcohol fraction boiling 70°-95° for the first catalyst was 266 cm<sup>3</sup>/l. of catalyst/hr. Qualitative analysis of the condensate disclosed the presence of considerable amounts of MeOH and 5% of the azeotropic mixture of iso-PrOH, PrOH, and iso-BuOH. 17 refs.

BOCHAROVA, E. M., DOLGOV, B. N., AND PETROVA, Y. N. [Synthesis of Higher Alcohols From Water Gas Under Pressure. II.] *See abs.* 279.

BOCHAROVA, E. M., DOLGOV, B. N., AND PROKHOROVA, Z. M. [Synthesis of Higher Alcohols From Water Gas Under Pressure. III.] *See abs.* 280.

BOCHAROVA, E. M., DOLGOV, B. N., AND KAN-KOGAN, K. I., AND PETROVA, Y. N. [Synthesis of Higher Alcohols From Carbon Dioxide and Hydrogen Under Pressure. V.] *See abs.* 282.

BOCHAROVA, E. M., DOLGOV, B. N., PETROVA, Y. N., AND YATSKOVSKAYA, N. S. [Synthesis of Alcohols of High Molecular Weight From Water Gas Under Pressure. IV. Rechecking of the Methods for Analysis of the Condensate.] *See abs.* 281.

BOCHIROU, L. *See abs.* 215.

BODE, K. *See abs.* 2921.

283. BONDENOFF, K. [Production, Application and Detection of Methanol and Isopropyl Alcohol.] *Apoth. Ztg.*, vol. 45, 1930, pp. 1141-1144; *Chem. Abs.*, vol. 25, 1931, p. 166.

Address dealing with both the earlier and present methods of manufacture, their various uses, and methods of detection.

BOENKNER, E. R. *See abs.* 2285.

284. BOEHM, E., AND BONHOEFFER, K. F. [Gaseous Reactions of Active Hydrogen.] *Ztschr. physikal. Chem.*, vol. 119, 1926, pp. 385-399; *Chem. Abs.*, vol. 20, 1926, p. 3645.

Reactions of H<sub>2</sub> activated by luminous discharge have been studied semiquantitatively for the following substances: O<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, NH<sub>3</sub>, Cl<sub>2</sub>, HCl, Br<sub>2</sub>, HBr, H<sub>2</sub>S, CH<sub>4</sub>, CO, CO<sub>2</sub>, and CH<sub>3</sub>Cl. The H<sub>2</sub> behaves as though it consisted of free atoms; with O<sub>2</sub> it forms directly H<sub>2</sub>O, with CO and CO<sub>2</sub> it forms small quantities of H<sub>2</sub>O. The halogens, which react very rapidly, form H halides. The active form of H is rapidly and completely destroyed by HCl, HBr, H<sub>2</sub>S, and CH<sub>3</sub>Cl, probably because of reactions like H+HCl=H<sub>2</sub>+Cl, N<sub>2</sub>+H<sub>2</sub>=NH<sub>3</sub>, and CH<sub>4</sub> are indifferent. Small quantities of O<sub>2</sub> increased the yield of active H<sub>2</sub> as they also increase the intensity of the Balmer spectrum; but the other gases tried had no effect.

285. BOENCKE, F. S. Equilibria in the Reduction of Chromium Oxide by Carbon, and Their Relation to the Decarburization of Chromium and Ferrochrome. Bureau of Mines Rept. of Investigations 3747, 1944, 34 pp.; *Chem. Abs.*, vol. 38, 1944, p. 3539.

Reduction of Cr<sub>2</sub>O<sub>3</sub> by C involves 4 distinct reversible-reaction steps: (1) 3Cr<sub>2</sub>O<sub>3</sub>+13C=2Cr<sub>3</sub>C+9CO; (2) 5Cr<sub>2</sub>O<sub>3</sub>+27Cr<sub>3</sub>C=13Cr<sub>7</sub>C<sub>2</sub>+15CO; (3) 5Cr<sub>2</sub>O<sub>3</sub>+14Cr<sub>7</sub>C<sub>2</sub>=27Cr<sub>7</sub>C+15CO; (4) Cr<sub>2</sub>O<sub>3</sub>+3Cr<sub>7</sub>C=14Cr+3CO. Describes apparatus and methods for measuring equilibria in these reaction steps, and thermodynamic values for each reaction are derived from equilibrium and requisite auxiliary-thermal data. The resulting thermal properties of the Cr carbides show that each carbide is stable with respect to dissociation into a lower carbide and C, into a higher carbide and Cr, or into the elements at all temperatures below the melting point of the carbide. The intermediate carbide is likewise stable with respect to dissociation into the other 2 carbides. A theoretical consideration is given of the decarburization of Cr and ferrochrome by Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>, and Si. Cr<sub>2</sub>O<sub>3</sub> is an effective decarburizing agent at 2,000°, particularly if means are furnished for operating under low CO partial pressures. Magnetite, theoretically, is a more effective decarburizer than Cr<sub>2</sub>O<sub>3</sub>, but in practice the rapid exchange of Fe in the refining agent with Cr in the metallic phase results in about the same net effectiveness as for Cr<sub>2</sub>O<sub>3</sub>. Both H<sub>2</sub> and Si are unsatisfactory agents for decarburizing Cr or ferrochrome.

———. *See abs.* 1729.

BOGOYAVLENSKAYA, A. N. *See abs.* 1806.

BOGOROV, A. *See abs.* 2174.

BOGUSLAVSKI, I. M. *See abs.* 1671.

BÖHM, H. *See abs.* 1711, 1713, 1717.

BÜKMANN, J. *See abs.* 3052, 3053.

BOLLHORN, A. *See abs.* 1504.

BOLTUS-GORNEANU, M. *See abs.* 659.

286. BOLZAT, W. [New Oils and Compounds for Metal Working.] *Oel u. Kohle*, vol. 39, 1943, pp. 416-418; *Chem. Zentrbl.*, 1943, II, p. 1433; *Chem. Abs.*, vol. 38, 1942, p. 1868.

Sulfonic acid obtained from hydrocarbons of the Fischer-Tropsch synthesis, Fettsaure D and its derivatives, and Emulgator II and M, are used for the preparing of water-soluble cutting oils. Oxidation products of synthetic paraffin wax are proposed as emulsifiers for the manufacture of cutting oils and drawing compounds. Emulgierwachs PS is less highly oxidized than Emulgierwachs PHS, and Emulgierwachs PVS is a saponified product.

BOZAR, F. See abs. 768, 3150, 3151, 3152.

BOZAR, H. F. See abs. 2731.

287. BONE, W. A. Discussion on Catalytic Reactions at High Pressures. *Proc. Roy. Soc. (London)*, vol. 127, A, 1930, pp. 240-267; *British Chem. Abs.*, 1930, A, p. 867.

Reviews work in the High-Pressure-Gas Research Laboratories at the Imperial College during the last 3 yr. with special reference to the formation of HCHO, MeOH, and CH<sub>4</sub> from CO and H<sub>2</sub>. By selecting a suitable catalyst and temperature any one of these 3 substances may be produced to the practical exclusion of the other 2. Absence of satisfactory equilibrium data in regard to the MeOH synthesis previous to the present series of investigations is pointed out, and the extreme importance of determining the equilibrium constant by approaching the equilibrium from both sides is emphasized. Discusses errors due to the fact that at the high pressures used the equilibrium mixtures do not obey the sample gas laws.

288. ———. High-Pressure Reactions. *Trans. Inst. Chem. Eng. (London)*, vol. 8, 1930, pp. 98-106; *Chem. Abs.*, vol. 26, 1932, p. 1168.

Recent applications of pressure in promoting useful chemical changes are reviewed with particular emphasis on the synthesis of NH<sub>3</sub> and catalytic syntheses from CO and H<sub>2</sub> mixtures. The influence of pressure upon gaseous explosions of CO-air and H<sub>2</sub>-air mixtures and the N<sub>2</sub> activation in CO-air explosions are also considered. Describes and illustrates equipment for a high-pressure research laboratory.

289. ———. Formation of Methanol by the Direct Oxidation of Methane. *Nature*, vol. 127, 1931, p. 481; *Fuel*, vol. 10, 1931, pp. 194-195; *Chem. Abs.*, vol. 25, 1931, p. 2968.

Studies on the slow combustion of C<sub>2</sub>H<sub>6</sub> showed that the initial product was not a peroxide but either EtOH or some less-oxygenated substance. It has now been found that direct oxidation of CH<sub>4</sub> at 360° and 100 atm. gives MeOH as the initial product. In mixtures of CH<sub>4</sub> and O<sub>2</sub> in the ratio of 9:1 the action was complete in a few minutes. About 17% of the CH<sub>4</sub> that was burned was recovered as MeOH, 0.6% as CH<sub>3</sub>O, and the remainder as CO, CO<sub>2</sub>, and H<sub>2</sub>O. No H<sub>2</sub> was liberated, and not even a trace of peroxide was formed. The MeOH was identified by conversion into HOC. H<sub>2</sub> CO<sub>2</sub> Me and p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me and was estimated as the nitrite.

290. ———. Initial Formation of Methyl Alcohol in the Oxidation of Methane. *Nature*, vol. 136, 1935, p. 910; *Chem. Abs.*, vol. 30, 1936, p. 1735.

Explosions of 5 CH<sub>4</sub>+2 O<sub>2</sub> mixtures yielded among the suddenly cooled products 0.18% MeOH and 0.03% HCHO. Not the faintest trace of peroxide formation could be detected. The MeOH is formed before the HCHO.

See abs. 2315.

291. BONE, W. A., AND ALLUM, R. E. Slow Combustion of Methane. *Proc. Roy. Soc. (London)*, vol. A134, 1932, pp. 578-591; *Chem. Abs.*, vol. 26, 1932, p. 2697.

Results of this investigation and of that summarized in abs. 2445, demonstrate a case of direct hydrocarbon oxidation, entirely uncomplicated by any sign of peroxidation, in which the most reactive mixture is that corresponding with the alcohol-forming proportion; substantial quantities of MeOH have actually been isolated in circumstances favoring its stability and survival, that is, chiefly at high pressure. The results fulfil the predictions of Bone's hydroxylation theory.

292. BONE, W. A., AND COWARD, H. F. Direct Union of Carbon and Hydrogen. I. Synthesis of Methane. *Jour. Chem. Soc.*, vol. 93, 1908, pp. 1975-1993; *Proc. Chem. Soc.*, vol. 24, 1908, p. 221; *Chem. Abs.*, vol. 3, 1909, p. 887.

Sugar charcoal was purified by prolonged ignition in dry Cl<sub>2</sub> first at 700° and then at 1,100°. The purity of the H<sub>2</sub> used was carefully tested. When less than 0.1 gm. of the charcoal is heated in a stream of pure, dry H<sub>2</sub> at 1,100°-1,200°, in an apparatus similar to that used by Bone and Jordan, abs. 296, large quantities of CH<sub>4</sub> were formed. On 2 separate experiments the yields obtained were 73%, the remainder being lost by unavoidable oxidation or decomposition in contact with the walls of the porcelain tube. In 1 group of 4 experiments, 422 cm<sup>3</sup> of CH<sub>4</sub> were obtained from 0.306 gm. of C. Results of the experiments by Bone and Jordan showing the formation of CH<sub>4</sub> from its elements are fully confirmed.

293. ———. Direct Union of Carbon and Hydrogen. II. Synthesis of Methane. *Jour. Chem. Soc.*, vol. 97, 1910, pp. 1219-1225; *Proc. Chem. Soc.*, 1910, vol. 26, p. 137; *Chem. Abs.*, vol. 4, 1910, p. 2938.

From less than 0.03 gm. of purified sugar charcoal, containing not more than 0.06% ash and less than 0.1% H<sub>2</sub>, not less than 95% CH<sub>4</sub> results by maintaining it in a stream of pure dry H<sub>2</sub> at 1,150° for 17-25 hr.

294. ———. Thermal Decomposition of Hydrocarbons. I. Methane, Ethane, Ethylene and Acetylene. *Jour. Chem. Soc.*, vol. 93-94, 1908, pp. 1197-1225; *Proc. Chem. Soc.*, vol. 24, 1908, p. 167; *Chem. Abs.*, vol. 2, 1908, p. 3061.

Results of a systematic investigation of the modes of decomposition of the 4 hydrocarbons 500°-1,200° were described. CH<sub>4</sub>, which is by far the most stable of the 4 hydrocarbons, and a principal product of the decomposition of the other 3, especially above 800°, decomposes for the main part into C and H<sub>2</sub>. The decomposition is, within the range investigated, a surface effect, and the C deposited is of a peculiarly hard and lustrous type. Decomposition of the other 3 hydrocarbons takes place chiefly throughout the main body of the gas, with formation of large quantities of CH<sub>4</sub>, which is explained on the supposition that residues such as =CH and =CH<sub>2</sub> (which may be considered to have momentary existence during the dissolution process), are directly hydrogenized in an atmosphere rich in H<sub>2</sub>. Assumption of the momentary formation of such residues (or the tendency to give rise to them, which actually becomes operative at moderately high temperatures) as the result of the initial dissolution of the hydrocarbon molecule, renders it possible to formulate a rational scheme of the chief causes at work and their modes of operation in each particular case. It may be supposed that these residues are capable of (a) forming H<sub>2</sub>C=CH<sub>2</sub> or HC≡CH as the result of encounters with other like residues, (b) breaking down directly into C and H<sub>2</sub>, (c) combining with H<sub>2</sub> to form CH<sub>4</sub>, and that all 3 possibilities may be realized simultaneously in proportions dependent on the temperature and the amount of H<sub>2</sub> present.

295. BONE, W. A., AND GARDNER, J. B. Comparative Studies of the Slow Combustion of Methane, Methyl Alcohol, Formaldehyde, and Formic Acid. *Proc. Roy. Soc. (London)*, vol. A154, 1936, pp. 297-328; *Chem. Abs.*, vol. 30, 1936, p. 4461.

The induction period in the slow combustion of CH<sub>4</sub> at 390°-420° (1) is not influenced by preheating the reactants or exposure of the reacting medium to ultra-violet light, (2) is lengthened by increasing the surface: volume ratio of a SiO<sub>2</sub> reaction vessel, (3) is shortest with a 2CH<sub>4</sub>+O<sub>2</sub> medium, (4) is characterized by the successive formation of small equilibrium amounts of MeOH and CH<sub>3</sub>O, and is greatly shortened by additions of either of them or of NO<sub>2</sub>, and (5) is markedly lengthened by additions of I. The slow oxidation of MeOH was much faster and less influenced by the SiO<sub>2</sub> surface than that of CH<sub>4</sub> at 390°. It shows no appreciable induction period but may be speeded up by small additions of CH<sub>3</sub>O or NO<sub>2</sub>. 2MeOH+O<sub>2</sub> is the most reactive medium, its end products being principally steam and the oxides of C, with a high CO:CO<sub>2</sub> ratio. A still higher oxidation rate was found for dry CH<sub>4</sub>, which showed no induction period even at 275°. HCO<sub>2</sub>H as well as performic acid and formaldehyde peroxide were formed as intermediate products. The slowest oxidation rate was observed with HCO<sub>2</sub>H, the gaseous end products being principally CO, CO<sub>2</sub>, steam, and H<sub>2</sub>. The results for CH<sub>4</sub> are explained on the basis of the hydroxylation theory. No sign of an initial preoxidation of the CH<sub>4</sub> was found in any of the experiments.

296. BONE, W. A., AND JERDAN, D. S. Direct Union of Carbon and Hydrogen. I. II. *Jour. Chem. Soc.*, vol. 71, 1897, pp. 41-61; *vol. 79, 1901, pp. 1042-1063.*

At a temperature of about 1,200° C. unites directly with H<sub>2</sub> to form CH<sub>4</sub>. No C<sub>2</sub>H<sub>2</sub> or other unsaturated hydrocarbons being formed. H<sub>2</sub> was passed over pure sugar C in a porcelain tube.

BONHOEFFER, K. F. See abs. 284.

BOONFIELD, L. W. See abs. 3151, 3152.

297. BOOMER, E. H. Natural Gas. Sci. and Ind. Research Council, Alberta, Canada. 9th Ann. Rept., 1928, pp. 51-53; *Chem. Abs.*, vol. 24, 1930, p. 4612.

Gas from the Viking field, containing CH<sub>4</sub>, 93%, C<sub>2</sub>H<sub>6</sub>, 8.5%, and N<sub>2</sub>, 3%, has been used as a raw material for thermal decomposition into C-black or low-boiling hydrocarbons. Direct oxidation processes are found to be of little value, but conversion into water gas has been achieved. Use of the gas for high-pressure synthesis is considered, and attention is being paid to the removal of S, which is present in large amount.

298. BOOMER, E. H., AND BROUGHTON, J. W. Oxidation of Methane at High Pressures. I. Preliminary Experiments. *Canadian Jour. Research*, vol. 15, B, 1937, pp. 375-382; *Chem. Abs.*, vol. 31, 1937, p. 8502.

Mixtures of O<sub>2</sub> and CH<sub>4</sub> at pressures 100-180 atm. were passed at various temperatures between 300° and 350° over various catalysts with the object of discovering the optimum conditions for the production of CH<sub>3</sub>OH. Preliminary experiments indicated that oxide catalysts were relatively inactive. Catalysts of the hopelite variety promoted oxidation violently for a short time and then became inactive. Cu and Ag catalysts were found to be the most desirable for the formation of CH<sub>3</sub>OH. O<sub>2</sub>-natural gas (largely CH<sub>4</sub>) mixture containing 7.3-7.5% O<sub>2</sub> were used. A maximum production of CH<sub>3</sub>OH was found to be a function of the rate of flow of the gas mixture. Small amounts of HCOOH and HCHO were obtained, the former appearing as HCOOCH<sub>3</sub> when Ag was the catalyst.

299. BOOMER, E. H., AND THOMAS, V. Oxidation of Methane at High Pressure. II. Experiments With

Various Mixtures of Viking Natural Gas and Air. *Canadian Jour. Research*, vol. 15, B, 1937, pp. 401-413; *Chem. Abs.*, vol. 32, 1938, p. 751.

Mixtures of a natural gas, substantially CH<sub>4</sub>, and air in various proportions were passed over catalysts, and the effects of the variables, composition of mixture, pressure, temperature, and space velocity were determined. Similar experiments were made with mixtures of CH<sub>4</sub> and air. Mixtures containing from less than 3% to more than 13% of O<sub>2</sub> as air were used. The temperature range was 350°-500°, and the pressure range 140-230 atm. MeOH was the principal product, and yields as high as 74% on the basis of C oxidized were obtained. Cu was the principal catalyst used. Traces of S poisoned the catalyst very effectively. The yield of useful products was found to depend primarily on the catalyst, the O<sub>2</sub> concentration, and the temperature. The influence of the time of reaction and the pressure was found to be slight. Low yields of HCHO and HCOOH and high yields of MeOH, when the oxidation was carried out under pressure and with a deficiency of O<sub>2</sub>, are explicable on the basis of the hydroxylation theory. Formation of peroxides was not observed.

300. ———. Oxidation of Methane at High Pressure. III. Experiments Using Pure Methane and Principally Copper as Catalyst. *Canadian Jour. Research*, vol. 15, B, 1937, pp. 414-437; *Chem. Abs.*, vol. 32, 1938, p. 751.

Mixtures of CH<sub>4</sub> containing some N<sub>2</sub> and O<sub>2</sub> were passed over Cu and Ag catalysts. The effects of the variables, composition of mixture, pressure, and temperature were determined. From 3-7% of O<sub>2</sub> was used in various experiments at pressures from 140-220 atm. at a temperature of 475°. The effect on yields of additions of CO<sub>2</sub> to the mixture was determined. Yields of MeOH up to 75% on the basis of C oxidized were obtained, but this is too low to be of commercial import since the yield of MeOH calculated on the basis of total C is less than 5%. O<sub>2</sub> loss in the conversion ranged from 50-10%. All the O<sub>2</sub> entering the system did not appear in the products, and nearly all experiments had O<sub>2</sub> in the off gases. Reactions are offered for the products observed based on Bone's hydroxylation theory and Norrish's chain reaction theory.

301. BOOMER, E. H., AND MORRIS, H. E. Hydrogen-Carbon Dioxide Reaction. *Jour. Am. Chem. Soc.*, vol. 54, 1932, p. 407; *Chem. Abs.*, vol. 26, 1932, p. 1180.

With an unsupported Zn-Cu-Al catalyst, a gas mixture of 27% CO<sub>2</sub>, 71% H<sub>2</sub>, and 2% N<sub>2</sub> at 325° and 1,700 lb. pressure gave an effluent gas containing 4% CO. This suggests that the primary step in the synthesis of MeOH from CO<sub>2</sub>-H<sub>2</sub> involves the reduction of CO<sub>2</sub> and the nature of the catalyst determines the extent to which the resultant CO is hydrogenated. As the activity of the catalyst decreases the MeOH reaction is most affected; experiments with this same catalyst and water gas gave appreciable amounts of CO<sub>2</sub>. This suggests a new mechanism for the synthesis of MeOH, which will be discussed later.

BOOMER, E. H., AND THOMAS, V. Oxidation of Methane at High Pressure. II. Experiments With Various Mixtures of Viking Natural Gas and Air. See abs. 299.

———. Oxidation of Methane at High Pressure. III. Experiments Using Pure Methane and Principally Copper as Catalyst. See abs. 300.

302. BOOMER, E. H., MORRIS, H. E., AND ARGUE, G. H. Apparent Formation of Copper Carbonyl. *Nature*, vol. 129, 1932, p. 438; *Chem. Abs.*, vol. 26, 1932, p. 2932.

Apparent formation of Cu carbonyl was noted in the synthesis of MeOH with a catalyst containing Cu.

This fact offers a new view on the mechanism of the synthesis of MeOH, which is to be presented later.

303. BOOTH, N. Chemicals From Carbonization Gases. I. Separation of Methane and Ethylene. II. Treatment of Methane and Ethylene. *Coke Smokeless-Fuel Age*, 1945, pp. 85-87, 112-114.

CH<sub>4</sub> may be decomposed by the action of heat with or without catalysts. Natural gas and steam passed over Fe, Ni, and Co oxides at 5,000 lb. and 500°-600° C. gave liquid hydrocarbon products. This process is not economically satisfactory unless the raw material is very cheaply obtained. The yield of products is only moderate under the best conditions so far found. CH<sub>4</sub> can be oxidized. For example, the reaction CH<sub>4</sub>+H<sub>2</sub>O→CO+3H<sub>2</sub> has been used to produce the gas for the Fischer-Tropsch synthesis: CH<sub>4</sub>+O<sub>2</sub>→CH<sub>3</sub>OH and CH<sub>4</sub>+O<sub>2</sub>→CO+2H<sub>2</sub>, the last reaction occurring over a Ni catalyst at temperatures of about 850°-1,200° C, the product again being useful for hydrocarbon syntheses.

See abs. 1628.

304. BOOTH, N., WILKINS, E. T., JOLLEY, L. J., AND TERNORTH, J. A. Catalytic Synthesis of Methane—Experimental Work of the Fuel Research Station. *Chem. Research Board*, Copyright Pub. 21/11, 1948, 44 pp.; *Chem. Abs.*, vol. 43, 1949, p. 3169.

Ni catalysts supported on kieselguhr and promoted with ThO<sub>2</sub> and MgO have been used with water gas-H<sub>2</sub> mixtures of varied compositions. In a laboratory-scale apparatus with a throughput of 1 cu. ft. of gas per hr. at atmospheric pressure, the catalysts enabled the conversion of over 99% of the CO in the process gas to be maintained for long periods with space velocities of 3,700 volumes of gas per volume catalyst space per hr. and at reaction temps. of 250°-350°. The performance of the catalysts was limited by a slow loss of activity, owing to poisoning by S compounds in the process gas and to deposition of C on the catalyst. The effect of the S compounds can be minimized by use of process gases containing less than 0.004 grain S/100 cu. ft. The deposition of C on the catalyst can be controlled by suitable conditions in the preparation of the catalyst, by the choice of suitable promoters and supports, by the use of 3H<sub>2</sub>:1CO ratio in the process gas, by additions of moderate proportions of water vapor to the process gas, and by effective removal of the exothermic heat of reaction so that high temperatures in the catalyst bed are avoided. Little, if any, advantage appeared to accrue from the use of 50 atm. pressure. Results in a unit processing 200 cu. ft. of gas per hr. were in substantial agreement with those in the laboratory unit. The best performance of the catalysts was equivalent to about 2,200 ton CH<sub>4</sub> per ton of catalyst used in experiments in which the catalyst was extended as a thin layer.

305. BORESKOV, G. K., AND SLIN'KO, M. G. Basis for Calculation of Catalyst Apparatus for Reversible Exothermic Processes. *Jour. Appl. Chem.* (U. S. S. R.), vol. 16, No. 9/10, 1943, pp. 377-396 (English summary); *Chem. Abs.*, vol. 38, 1944, p. 6135.

Mathematical theoretical-design data. It is shown that for calculation of optimum temperature, it is enough to know the apparent activation energy of the forward reaction. Graphical and analytical methods of determination of optimum temperature are presented. Shows graphic calculation method by determination of the catalyst mass necessary for changing the degree of contact under different heat-flow conditions.

BORESENKO, A. I. See abs. 3413, 3414.

306. BORISOV, P. B., AND EVENTOVA, M. S. [Production of Gasoline from Paraffin Residues from Synthine in the Presence of Aluminum Chloride.] *Neftyanoe Khoz.*, vol. 20, No. 12, 1939, pp. 43-45; *Khim. Referat.*

Zhur., No. 6, 1940, p. 110; *Chem. Abs.*, vol. 36, 1942, p. 4994.

Liquid fraction, boiling, 240°-300°, of synthine residue and the solid fraction requires 20% of AlCl<sub>3</sub> for cracking. The solid-fraction boiling above 300° is cracked with only 10% of AlCl<sub>3</sub>. Maximum yields of gasoline, up to 48%, are obtained on cracking with 15% AlCl<sub>3</sub>. The gasoline obtained, boiling 22°-150°, consists nearly exclusively of isoparaffins. The octane number of the 22°-50° fraction containing pentanes and hexanes is 88, of the 50°-100° fraction it is 73, and of the whole 22°-150° fraction it is 79.

BORISOVA, G. P. See abs. 2169.

BORMANN, W. See abs. 2929, 2930, 2931, 2934.

307. BOSCH, C. [Problems of Commercial Hydrogenation Processes.] *Chem. Fabrik*, vol. 7, 1934, pp. 1-10; *Chem. Abs.*, vol. 28, 1934, p. 1424; *British Chem. Abs.*, 1934, B, p. 256.

Hydrogenation of N<sub>2</sub> to NH<sub>3</sub>, CO to alcohols, and coal, petroleum, and tar to benzene as developed by the I. G. Farbenindustrie A.-G. presented in an address.

308. ———. Where There's a Will, There's a Way. *Ind. Chemist*, vol. 10, 1934, pp. 90-94, 113.

Abridged version of a lecture before the Norwegian Academy of Science in which the author discusses the problems arising during the development from the laboratory to the technical scale of the processes carried out in the works of I. G. Farbenindustrie A.-G., namely hydrogenation of N<sub>2</sub> to NH<sub>3</sub>, of CO to MeOH, and of coal or tar to gasoline. The principal items dealt with are the production and purification of H<sub>2</sub>, the development of suitable catalysts, and the selection of constructional materials of high chemical resistance.

309. BOSWORTH, R. C. L. Synthetic Fuels From Carbon Monoxide and Hydrogen. *Australian Jour. Sci.*, vol. 5, 1942, pp. 28-33; *Chem. Abs.*, vol. 37, 1943, p. 741.

Production of synthetic fuels by catalytic reduction of CO with H<sub>2</sub>.

310. BOTOLFSSEN, E. [Studies of Catalysts.] *Arch. Math. Naturvidensk.*, vol. B41, pt. 2, No. 7, 1938, p. 29.

1. Water-gas reaction. The effect of MgCO<sub>3</sub> and MgO, alone and as carriers for other catalysts, on the course of the water-gas reaction is studied at temperatures 300°-800°. 2. CH<sub>4</sub> formation in CO-steam mixtures. A catalyst obtained by precipitation from Ni nitrate solution forms CH<sub>4</sub> from CO-H<sub>2</sub>O mixtures at temperatures at which formation of H<sub>2</sub> does not yet occur. 3. Decomposition of CO in CO-steam mixtures. The catalyst described yields from this mixture a gas containing no CO. The reaction, separating out C, begins at 150° and is complete at 190°-195°. 4. Formic-acid formation in CO-steam mixtures. HCOOH formation can be regarded as an intermediate stage of the water-gas reaction. 5. Ni carbonyl as catalyst.

See abs. 2583.

311. BOUDOUARD, O. [Decomposition of Carbonic Anhydride in Presence of Carbon.] *Compt. rend.*, vol. 128, 1899, pp. 824-825; *Jour. Chem. Soc.*, vol. 2, 1899, p. 417.

When CO<sub>2</sub> is heated at 650° with charcoal and with C from the decomposition of CO, the proportion of CO in the gas gradually increases, the reaction being more rapid with the charcoal than with the C. The limit of the reaction with charcoal was reached after 12 hr., and the composition of the gaseous mixture (CO, 61 vol., CO 39 vol.), is identical with the composition of the gas at the limit of the reaction between CO and Co oxide at the same temperature.

312. ———. [Decomposition of Carbonic Anhydride in Presence of Carbon.] *Compt. rend.*, vol. 128, 1899, pp. 1524-1525; *Jour. Chem. Soc.*, vol. 2, 1899, p. 596.

Reaction between CO<sub>2</sub> and C at 800° and 925° has been studied. Different forms of C were used. The speed of reaction was greatest with wood charcoal and least with bone black. As is the case at 650°, at 800° the decomposition ceases when the composition of the gaseous mixture is the same as that obtained by the action of CO on Ni or Co oxide at the same temperature, in this case, 7% of CO<sub>2</sub> and 93% of CO. At 925° the proportion of CO<sub>2</sub> is 4%.

313. ———. [Decomposition of Carbonic Oxide by Metallic Oxides.] *Compt. rend.*, vol. 128, 1899, pp. 1522-1523; *Bull. soc. chim.*, vol. 21, 1899, pp. 463-465, 712-713; *Jour. Chem. Soc.*, vol. 2, 1899, p. 595.

When CO is decomposed at 800° in presence of oxide of Ni or Co or of Fe<sub>2</sub>O<sub>3</sub>, the amount of decomposition depends on the time of reaction. The speed of reaction at 800° is greater than at 650°, equilibrium being attained in 2 hr. at the higher temperature and only after 6 hr. at the lower. In the presence of Ni or Co oxide at 800°, no further change occurs after the gaseous mixture contains 7% of CO<sub>2</sub> and 93% of CO.

314. ———. [Decomposition of Carbonic Oxide in Presence of Ferric Oxide.] *Compt. rend.*, vol. 128, 1899, pp. 98-101; *Jour. Chem. Soc.*, vol. 2, 1899, p. 287.

When finely divided ferric oxide is heated at 445° in sealed tubes with pure and dried CO, the decomposition of the latter is a function of the time and of the quantity of ferric oxide present. The quantity of CO<sub>2</sub> formed increases regularly and eventually the decomposition is complete. Similar experiments are being made with Co and Ni oxides at 445° and with all 3 oxides at higher temperatures.

315. ———. [Decomposition of Carbonic Oxide in Presence of Metallic Oxides.] *Compt. rend.*, vol. 128, 1899, pp. 307-309; *Jour. Chem. Soc.*, vol. 2, 1899, p. 365.

When CO is passed over heated Ni and Co oxides at 445°, the rate of oxidation is much more rapid than with ferric oxides, as in the latter case the amount of decomposition increases with the quantity of oxide used and with the time. In all these cases the amount of C deposited is of the same order of magnitude as the oxide employed. When a large excess of purified C is mixed with the oxide, the results are the same but the action appears to take place more slowly.

316. ———. [Decomposition of Carbonic Oxide in Presence of Metallic Oxides.] *Compt. rend.*, vol. 128, 1899, pp. 822-824; *Jour. Chem. Soc.*, vol. 2, 1899, p. 417.

Decomposition of CO at 650° in presence of Fe<sub>2</sub>O<sub>3</sub>, Ni<sub>2</sub>O<sub>3</sub>, and Co<sub>2</sub>O<sub>3</sub> is a function of the time and within certain limits depends on the quantity of metallic oxide present. Whereas at 445° the decomposition is complete, at 650° it is limited, and in presence of Co<sub>2</sub>O<sub>3</sub> decomposition ceases when the gaseous mixture contains 61% CO<sub>2</sub> and 39% CO.

317. ———. [Influence of Pressure in Phenomena of Chemical Equilibrium.] *Compt. rend.*, vol. 131, 1900, pp. 1204-1206; *Jour. Chem. Soc.*, vol. 2, 1901, p. 151.

It has been shown that the reaction CO<sub>2</sub>+C=2CO proceeds as a reversible reaction in accordance with dynamical deductions (see abs. 318). Experiments previously conducted at atmospheric pressure are now supplemented by determinations at lower pressure, which are wholly in accord with the previous results and again verify the formula given there.

318. ———. [Numerical Laws of Chemical Equilibrium.] *Compt. rend.*, vol. 130, 1900, pp. 132-134; *Jour. Chem. Soc.*, vol. 2, 1900, p. 199.

In a gaseous system in equilibrium at all temperatures and pressures a relation exists between the concentrate of the various gaseous phases. In the case of the system 2CO=CO<sub>2</sub>+C the final equilibrium does not depend on the initial state between 650° and 800°. From an equation set up, the ratios of the concentrate of CO and CO<sub>2</sub> at various temperatures may be calculated and agreement with experimental determinations may be seen:

Temperature	CO <sub>2</sub> found	Calculated	CO found	Calculated
650°	0.61	0.61	0.39	0.39
800°	0.07	0.10	0.93	0.90
925°	0.04	0.03	0.96	0.97

319. ———. [Chemical Equilibria.] *Ann. chim. phys.*, ser. 7, vol. 24, 1901, pp. 5-85; *Jour. Chem. Soc.*, vol. 2, 1901, p. 646.

Résumé of earlier papers containing a full discussion of the reversible reaction 2CO=CO<sub>2</sub>+C. In the presence of finely divided metallic substances such as Fe heated at 445°, the velocity of the direct reaction is increased without modifying the proportions of the gaseous reagents in the final system when equilibrium is attained. The experiments prove that the equilibrium ratio CO:CO<sub>2</sub> in contact with C is a function of the temperature, and the results are in general agreement with the laws respecting equilibria in gaseous systems.

320. ———. [Reducing Action of Carbon on Metallic Compounds.] *Bull. soc. chim.*, ser. 3, vol. 25, 1901, pp. 282-287; *Jour. Chem. Soc.*, vol. 2, 1901, p. 314.

Reduction of metallic compounds by heating with pure C at temperatures of 445°-1,150° is not due directly to C but to CO, a trace of which is always present to start the reaction. The CO<sub>2</sub> formed is then decomposed by C with the regeneration of CO and so on indefinitely. The results are in accord with the reaction 2CO=CO<sub>2</sub>+C.

321. ———. Reversible Reaction CO<sub>2</sub>+H<sub>2</sub>=CO+H<sub>2</sub>O. *Bull. soc. chim.*, vol. 25, 1901, pp. 484-489; *Jour. Chem. Soc.*, vol. 2, 1901, p. 383.

Mixture of equal volumes of dry CO<sub>2</sub> and H<sub>2</sub> was heated in a porcelain vessel at 850° and 1,100°, and an analysis was made of the mixture of CO<sub>2</sub>, CO, H<sub>2</sub>, and aqueous vapor produced. The results agree fairly well with Le Chatelier's formula (see abs. 318) for the equilibrium of gaseous mixtures. Pressure has no influence on the equilibrium since the numbers of reacting and produced molecules are equal. The reaction is of interest in connection with the manufacture of water gas.

BOUNDY, R. H. See abs. 1363.

BOWEN, A. R. See abs. 2368.

BOWMAN, N. J. See abs. 420b, 3642b.

BOYD, C. A. See abs. 1428.

322. BOYN, J. Petroleum Industry Has Definite Role in Synthetic Development. *Petrol. Refiner*, vol. 29, No. 12, 1950, pp. 77-85.

Barring unexpected developments in atomic or solar energy, an anticipated gap between domestic oil demand and supply will have to be met by synthetic liquid fuels and imports. Although the amounts of oil ultimately recovered from domestic oil fields will be far greater than present proved reserves, it is obvious that the security of the Nation's liquid-fuels position will be greatly enhanced when the supply is based in part on solid fuels, such as coal and oil shale, which compose more than 95% of our proved fuel reserves. Synthetic fuel processes also can play an important part in meeting requirements for strategic chemicals. Current

shortages and increasing requirements for benzene, phenol, toluene, and certain other chemicals could accelerate the schedule for constructing the initial coal-hydrogenation plants, in view of the fact that these chemicals would be produced from such plants in important quantities.

323. ———. Synthetic Fuels Future. *Oil Gas Jour.*, vol. 49, No. 28, 1950, p. 184; *Petrol. Refiner*, vol. 29, Dec. 1950, pp. 77-85.

Research on synthetic fuels has progressed to the point where it has set a ceiling on the prices of petroleum products, and the time may not be far distant when economic considerations will bring about a substantial synthetic-fuels industry. The oil industry is the logical one to handle this business, particularly after the coal or oil shale is brought above ground and a gradual shift of some parts of the liquid-fuels market to synthetics is predicted. Domestic and foreign supplies of crude petroleum are briefly analyzed and figures on costs and capital investment for synthetic fuels are cited.

324. ———. Changing Patterns of Fuel Supply. *Mech. Eng.*, vol. 73, 1951, pp. 189-190; *Chem. Abs.*, vol. 45, 1951, p. 3143.

The actual quantity of coal produced has remained relatively unchanged for some time, but the % of our fuel requirements supplied by coal has declined from over 78% in 1920 to less than 40% in 1949, while that of petroleum has increased from 15% to almost 37% and natural gas from 4% to almost 19% in the same period. Petroleum production and reserves of gas and oil have increased and further reserves will be found, but the gap between production and consumption will be narrowed so that there must be recourse to synthetic fuels, especially gasoline from coal. High yields of aromatic hydrocarbons can be secured both in the hydrogenation of coal and by suitable treatment of oil shale.

325. BOYER, J. [Industrial Syntheses of Methanol.] *La Nature*, No. 3137, 1947, pp. 177-180.

Synthesis gas for the production of MeOH is produced by the gasification of wood in the presence of O<sub>2</sub> and steam, yielding a synthesis gas with a H<sub>2</sub>:CO ratio of 2:2 and 7% of inerts. The gas is converted by means of the Grande Paroisse process using a mixture of ZnO and Cr<sub>2</sub>O<sub>3</sub> as the catalyst at 425° and 650 kgm. per cm.<sup>2</sup> pressure. After rectification the MeOH obtained is 99.9% pure. The yield per ton of dry wood is 3 hl.

BRADFORD, B. W. See abs. 341.

BRADLEY, T. F. See abs. 2241, 2442.

BRAMLEY, A., AND BEEBY, G. H. Gaseous Cementation of Iron and Steel. II. Cementation With the Nitrogenous Vapors of Pyridine and Methyl Cyanide. See abs. 327.

326. BRAMLEY, A., AND JINKINGS, A. J. Gaseous Cementation of Iron and Steel. I. Cementation by Carbon Monoxide. *Iron and Steel Inst. Carnegie Schol. Mem.*, vol. 15, 1926, pp. 17-69; *Chem. Abs.*, vol. 21, 1927, p. 1622.

Carburizing action of CO is studied by placing test bars in a SiO<sub>2</sub> tube, glazed inside and out and heated with Nichrome wire, the gas being generated by the action of concentrated H<sub>2</sub>SO<sub>4</sub> on HCOOH. Preliminary experiments showed that it was necessary periodically to reverse the direction of flow of the gas and support the bars centrally in the furnace tube to obtain uniform carburization. Thoroughly dry gas was essential. A detailed study was made of the amount and distribution of C introduced during the process of cementation, as affected by (a) the rate of flow of the gas through the furnace, (b) the period of carburization, (c) the temperature of carburization, (d)

the concentration of C in the original steel. Curves and photomicrographs are shown. No evidence of the liquation described by Giolitti was found. In the low-C steels the increases in diameter are in the same order as the weight of C introduced. In the bars carburized below 900° and those originally containing considerable amounts of C, the changes in dimensions were small.

327. BRAMLEY, A., AND BEEBY, G. H. Gaseous Cementation of Iron and Steel. II. Cementation With the Nitrogenous Vapor of Pyridine and Methyl Cyanide. *Iron and Steel Inst. Carnegie Schol. Mem.*, vol. 15, 1926, pp. 71-125; *Chem. Abs.*, vol. 21, 1927, p. 1622.

Object is to ascertain the amount and distribution of both C and N introduced when the bars were heated in an atmosphere of CO saturated at 18° with the vapors of either pyridine or MeCN. The CO is passed up a column down which the liquid containing the vapor with which the gas is to be saturated is kept dripping through Cu gauze. Otherwise the equipment is the same as in Part I. The following factors were studied for CO saturated with C<sub>2</sub>H<sub>5</sub>N: (a) Rate of flow of gas stream; (b) period of cementation; (c) temperature of cementation. MeCN is a more efficient cementing agent than C<sub>2</sub>H<sub>5</sub>N. The condition of the bars after cementation was similar to that obtained with C<sub>2</sub>H<sub>5</sub>N. The effect of increasing initial concentration of C was studied both for CO+C<sub>2</sub>H<sub>5</sub>N and CO+MeCN. In the presence of N compounds, the importance of reversing the direction of gas flow is greater than with CO alone, as even in this case the cementation was at times more intense at the ends than in the middle of the bars. Photomicrographs show that a characteristic feature of a case produced by a nitrogenous cement is the presence of a narrow zone near the inner edge of the case in which fairly deep etching shows needles. The presence of N also reduces the amount of C in the steel of eutectoid composition and tends to preserve the Fe in the  $\gamma$  state.

328. BRAMLEY, A., AND LAWTON, G. Gaseous Cementation of Iron and Steel. III. Influence of Hydrocarbons on the Carburization of Iron and Steel. *Iron and Steel Inst. Carnegie Schol. Mem.*, vol. 16, 1927, pp. 35-100; *Chem. Abs.*, vol. 22, 1928, p. 207.

From a study of photomicrographs, it is concluded that the cementation produced when a carburetted gas (such as CO saturated with toluene at 18°) is passed over a specimen of Fe or steel in 1 direction only is much more uneven than when CO is used alone. Obstructions to the free circulation of carburizing gas cause uneven cementation. Alternate passing of the gas, first in 1 direction and then in the opposite, favors even cementation. The fact that the carburizing gas is often of such a nature as to be decomposed by the heat of the furnace must be taken into account if even cementation is desired. Variations from this source will depend upon the temperature and size of the various parts of the furnace and upon the decomposition. When a tubelike furnace is used and gas is passed in from both ends the cementation is often considerably weaker in the center of the bars than at the ends. This is because the carburizing agent becomes exhausted too quickly and indicates either too slow a flow of gas or excessive decomposition of the latter. Under certain conditions the decomposing gas deposits a sheath of C over the ends of the bars. This sheath prevents contact of gas and metal and further carburization at these points is difficult. Such bars show a greater cementation along their centers. The authors prove that the liquation theory of cementation as put forth by Giolitti is unsound. They find that the amount of redistribution of the C in steel, while the latter is cooling down, is inappreciable. The depth of carburization is greater

the longer the period of cementation and the higher the temperature. The depth increases with the temperature according to a linear law. As the period of cementation is increased in geometrical progression, the depth of penetration increases in the same way but with a different common ratio. The diffusivity constants for C diffusing into steel are calculated for the several carburizing mixtures and temperatures employed.

329. BRAMLEY, A., AND TURNER, G. Gaseous Cementation of Iron and Steel. IV. Action of Mixtures of Carbon Monoxide and Ammonia on Iron and Steel and Its Bearing on the Process of Cementation. *Iron and Steel Inst. Carnegie Schol. Mem.*, vol. 17, 1928, pp. 23-66; *Chem. Abs.*, vol. 22, 1928, p. 4437.

Cementations of Armco Fe were made at various temperatures with mixtures of CO and NH<sub>3</sub> and with mixtures of CO and H<sub>2</sub>. The cementations were conducted at various temperatures ranging 700°-1,050° at intervals of 50°, and the process was continued in each case for 10 hr. The test results prove that the carburizing action of mixtures of CO and NH<sub>3</sub> is much greater than that of CO alone. The carburizing properties of mixtures of CO and H<sub>2</sub> were stronger than CO alone but not so intense as corresponding mixtures containing NH<sub>3</sub>. Micrographs show that the microstructure of the Fe-C alloys is entirely altered by the presence of N; this is the case especially when the cementations are made at temperatures below 800°; above 800° very marked segregation of cementite takes place.

BRAMLEY, A., AND LAWTON, G. Gaseous Cementation of Iron and Steel. III. Influence of Hydrocarbons on the Carburization of Iron and Steel. See abs. 328.

330. BRAMLEY, A., AND LORD, H. D. Equilibria Between Mixtures of Carbon Monoxide and Carbon Dioxide at Various Pressures in Contact With Steels of Different Carbon Concentrations at 750°-1,150°. *Jour. Chem. Soc.*, 1932, pp. 1641-1669; *Chem. Abs.*, vol. 26, 1932, p. 5529.

Equilibria between CO, CO<sub>2</sub>, and steels of C contents varying from 0.1 to 2.0% have been measured at temperatures of 750°-1,150° by means of a static method. Results indicate that C in austenite is in the form of an equilibrium mixture of monatomic C and FeC. The concentration of C in the gaseous mixture follows Henry's law if the C vapor is considered monatomic. At the 700°-1,100°, graphite is the stable form of C and not FeC. In the presence of graphite, further carburization will occur if the CO:CO<sub>2</sub> ratio is less than 1; if it is greater than 1, decarburization will occur. In the equilibrium diagram, the graphite-solubility line is approximately parallel to the Fe<sub>3</sub>C-solubility line and to the left of that of amorphous C. Heats of formation were determined as follows: Dissolved FeC from 3Fe+2CO 29,950 cal.; precipitated FeC from 3Fe+2CO 36,950 cal.; FeC from  $\gamma$ -iron and graphite -4,750 cal.; and FeC from  $\alpha$ -iron and graphite -6,950 cal.

BRAMLEY, A., AND TURNER, G. Gaseous Cementation of Iron and Steel. IV. Action of Mixtures of Carbon Monoxide and Ammonia on Iron and Steel and Its Bearing on the Process of Cementation. See abs. 329.

BRANTING, B. F. See abs. 3209.

331. BRATZLER, K. [Sorption Methods for the Analytical and Preparative Separation of Gases.] *Oel u. Kohle*, vol. 39, 1943, pp. 953-960; *Chem. Abs.*, vol. 38, 1944, p. 6154.

Briefly discusses theory of the separation of gases by adsorption and desorption. Because of the lowered vapor pressure of the adsorbed gases the difference in

the relative volatility of various adsorbed gases becomes great enough for purposes of separation at temperatures that would be too high for effective separation by fractional distillation. Pure C<sub>2</sub>H<sub>6</sub> is obtained from the commercial gas containing C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> by passing it slowly at 0° or room temperature over activated charcoal that had been degassed at 200° and 0.1 mm. Hg. After atmospheric pressure has been reached, which may require 20-30 min., an electric oven is placed over part of the adsorption tube and some of the gas is desorbed; the desorbed gas comes in contact with the adsorbed gas in the cold part of the tube and exchange of the heavier and lighter components of the gas takes place. In this way the light impurities are driven off first followed by pure C<sub>2</sub>H<sub>6</sub>, and the heavy impurities remain adsorbed. The same principle is applied to analytical methods that give satisfactory results if allowance is made for the material that remains adsorbed. This difficulty is avoided by carrying out the desorption under vacuum. The latter method is particularly suited to the determination of small concentrations of a volatile component in a less volatile gas (C<sub>2</sub> hydrocarbons in commercial C<sub>3</sub>H<sub>8</sub>). For the determination of C<sub>2</sub> and C<sub>3</sub> hydrocarbons in coke-oven gas or residual gas from the adsorption plant connected with a Fischer-Tropsch synthesis plant, it is best to concentrate these compounds by adsorption on activated charcoal and desorb them by steaming (Carbotox process). If the hydrocarbon mixture to be adsorbed contains olefins, the breakthrough of olefins, and thereby of the other hydrocarbons through the adsorbent, can be controlled automatically by bromination of the olefins with Br made in an electrolytic cell and measuring the amount of current used in the preparation of Br.

331a. ———. [Technical Production of Low-Boiling Hydrocarbons.] *Erdöl u. Kohle*, vol. 4, 1951, pp. 478-486; *Fuel Abs.*, vol. 10, No. 6, 1951, abs. 5143.

Processes for large-scale hydrocarbon production over past 30 yr. are chronologically briefly reviewed (decomposition of coke-oven gas, natural gas processes, high-pressure hydrogenation, Fischer-Tropsch synthesis, and various petroleum cracking processes). Details and flow sheets are given of processes for conversion of high-pressure hydrogenation waste gases to C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub>, and production of C<sub>2</sub>H<sub>4</sub> from coke-oven gas. Descriptions and flow sheets are also given of batch production of gas oil and gasoline from Fischer-Tropsch waste gases and of continuous hyper-sorption and rectification processes. Disadvantages and operational difficulties of the various methods are discussed.

BRAUDE, G., AND BRUNS, B. [Kinetics and Mechanism of the Catalytic Hydrogenation of Carbon Monoxide. II. Formation of Iron Carbide During Hydrogenation of Carbon Monoxide on an Iron Catalyst.] See abs. 333.

332. BRAUDE, G., SHURMOVSKAYA, N., AND BRUNS, B. [Kinetics and Mechanism of the Catalytic Hydrogenation of Carbon Monoxide. I. Method of Preparation of Metal Catalysts From Oxides and Handling the Catalysts Without Contact With the Air.] *Jour. Phys. Chem. (U. S. S. R.)*, vol. 22, 1948, pp. 483-486; *Chem. Abs.*, vol. 42, 1948, p. 7147.

Reduced metal is kept in H<sub>2</sub>. Samples are withdrawn in H<sub>2</sub> also.

333. BRAUDE, G., AND BRUNS, B. [Kinetics and Mechanism of the Catalytic Hydrogenation of Carbon Monoxide. II. Formation of Iron Carbide During Hydrogenation of Carbon Monoxide on an Iron Catalyst.] *Jour. Phys. Chem. (U. S. S. R.)*, vol. 22, 1948, pp. 487-494; *Chem. Abs.*, vol. 42, 1948, pp. 7147-7148.

Mixtures of CO and H<sub>2</sub> in the ratios 1:3 to 1:5 were circulated at 225°-350° over an Fe catalyst prepared

by H<sub>2</sub> reduction of Fe<sub>3</sub>O<sub>4</sub>. The main reaction occurring was  $n\text{Fe} + \text{CO} + \text{H}_2 \rightarrow \text{Fe}_n\text{C} + \text{H}_2\text{O}$  (1). This was proved by the following observations: (a) The gas pressure dropped first (for example, for 5 min.) rapidly and then very slowly. The rapid drop (after cooling the reaction product) corresponded to twice the original amount of CO. (b) The reaction product was mainly H<sub>2</sub>O, and the amount of CH<sub>4</sub> and CO<sub>2</sub> formed was too small to account for the CO consumed. (c) The missing C was found in the catalyst. When the catalyst was used for longer time, the concentration of C in it increased and its efficiency decreased; the catalytic activity almost disappeared when 0.24 atom C was deposited/atom Fe. The slow drop of pressure was due to the reaction between this carbide and the excess of H<sub>2</sub>. The rate of reaction I increased 2.5 times when the initial pressure of CO was raised from 20 to 241 mm. dibutyl phthalate and was about proportional to the square root of the H<sub>2</sub> pressure (46-1.103 mm. dibutyl phthalate). The energy of activation (from the temperature coefficient) of reaction I was 15,500 cal./mol. The formation of CH<sub>4</sub> is due to the reaction  $n\text{Fe} + 2\text{CO} \rightarrow \text{Fe}_n\text{C} + \text{CO}_2$ . This reaction was studied in the absence of H<sub>2</sub>. It follows the equation of the first order, is slower than I, and has an apparent energy of activation (264°-350°) of 6,900 cal./mol. The mechanism of the hydrogenation of CO is discussed.

BRAUDE, G. E. See abs. 1591, 1592.

334. BRAUNHOLZ, W. T. K. Rational Utilization of Coal. Fuels Obtained by the Treatment of Coal. *Colliery Guard*, vol. 138, 1929, pp. 341-343; *Chem. Abs.*, vol. 23, 1929, p. 1736.

General discussion of carbonization and hydrogenation of solid fuels and synthesis of liquid fuels from water gas as a means of obtaining more suitable fuels from coal.

335. BRAUNKOHL-BENZIN, A.-G. [Improving the Effect of Cobalt Catalyst in Hydrocarbon Synthesis.] *German Patent Abstracts*, vol. 64, 1943, p. 726; *British Coal Utilization and Research Assoc. Monthly Bull.*, vol. 8, 1944, abs. S805.

Addition of a relatively large amount of steam to the synthesis gas when starting up for the first time is claimed to have a beneficial effect upon the Co catalyst.

336. BRAYBROOK, F. H. Development of Synthetic Detergents and Future Trends. *Chem. and Ind.*, 1948, pp. 404-407, 409-410.

Growth of the synthetic-detergent industry is traced and statistics are quoted. In the United States alone for 1947, it is believed that 150,000 tons (35-40% active content), or 7.5% of the American soap market, were sold. Assuming that 1 ton of synthetic soap (20% active content) replaces 1 ton of fatty-acid soap (60% fatty acid content), there is already a replacement of 15% of the United States soap market by synthetic detergents. The trend in Germany during the war years was away from the use of natural fatty acids in soap manufacture to the use of synthetic detergents based on nonfatty raw materials. The chief raw materials, therefore, were the oxidation products of Fischer-Tropsch paraffin wax or gatsch or the wax obtained by the hydrogenation of brown coal. The main concentration of effort was toward the production of the alkyl sulfonates, commonly known as Mersolates, prepared by the sulfochlorination of the Fischer-Tropsch paraffins. The total output reached 85,000 tons per annum (calculated as 100% active matter) from both I. G. Farbenindustrie factories at Leuna and Wolfen, the equivalent of probably 170,000 tons of the prewar marketed soap. The future trend is evident: an increasing consumer demand for edible fats, with a decreasing utilization of natural fats for the

manufacture of soap and an increasing demand for synthetic detergents from nonfatty oil raw materials for which petroleum and synthesis products are the obvious sources.

337. BREDIG, G., AND ALLOLIO, R. [X-Ray Studies of Catalytically Active Metals.] *Ztschr. physik. Chem.*, vol. 126, 1927, pp. 41-71; *Chem. Abs.*, vol. 21, 1927, p. 2204.

Pt and Pd surfaces obtained by the glow discharge in H<sub>2</sub> at low pressures have been shown to be of very slight or negligible activity as catalysts for the hydrogenation of C<sub>2</sub>H<sub>4</sub> or for the combination of H<sub>2</sub> and O<sub>2</sub>. These metal preparations contain considerable amounts of H<sub>2</sub> as evidenced by X-ray photographs, the presence of which in the metal lattice is responsible for lack of activity. Ni, similarly prepared, is inactive at 350° in the hydrogenation of C<sub>2</sub>H<sub>4</sub>. When Pt and Pd are prepared as above but in O<sub>2</sub> at low pressures, very active surfaces are obtained. X-ray studies of these active Pt, Pd, and Ni surfaces have shown that except for differences in particle size, there is no difference between the finely divided, highly active, and the compact, slightly active metals.

338. BREDIG, G., AND CARTER, S. R. [Catalytic Synthesis of Formic Acid Under Pressure.] *Ber. deut. chem. Gesell.*, vol. 47, 1914, pp. 541-545; *Chem. Abs.*, vol. 8, 1914, p. 1584.

Object of this work was to determine: (1) Whether the equilibrium in the formation of HCO<sub>2</sub>H from ordinary H<sub>2</sub> and CO<sub>2</sub> could be materially shifted in favor of the HCO<sub>2</sub>H formation by sufficiently decreasing its partial pressure, and (2) whether the reaction velocity could be increased enough by the use of a suitable catalyst and of high pressures. Below are given, respectively, the weight of substance used in 200 cm.<sup>3</sup> H<sub>2</sub>O, the gas pressure, the time, and the yield of formate in % of the theoretical amount that would have been formed if all of the carbonate, or borax had been converted into formate. In all cases but (1), where no catalyst was used, 1.5 gm. Pd sponge was employed, and the temperature was 70° except in (3) where it was 95°. (1) 10 gm. KHCO<sub>3</sub>, 60 atm. H<sub>2</sub>, 24 hr., 0.6%. (2) 10 gm. KHCO<sub>3</sub>, 60 atm. H<sub>2</sub>, 23 hr., 74.7%. (3) 10 gm. KHCO<sub>3</sub>, 30 atm. H<sub>2</sub>, 26 hr., 60.3%. (4) 0.4 gm. CaCO<sub>3</sub>, 50 atm. H<sub>2</sub>+20 atm. CO<sub>2</sub>, 4.5 hr., 100%. (5) 9.5 gm. Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O, 30 atm. H<sub>2</sub>+30 atm. CO<sub>2</sub>, 16 hr., 21.7%. (6) 10.6 gm. Na<sub>2</sub>CO<sub>3</sub>, 60 atm. H<sub>2</sub>, 7 hr., 0.4%. The negligible yield with Na<sub>2</sub>CO<sub>3</sub>, in spite of its stronger alkalinity, as compared with that obtained with KHCO<sub>3</sub>, would indicate that the velocity and free energy of the HCO<sub>2</sub>H formation rises and falls not only with the partial pressure of the H<sub>2</sub> but also with that of the CO<sub>2</sub>. The small yield with KHCO<sub>3</sub> but without Pd shows that the method is really catalytic.

339. [Equilibrium of the Reduction of Carbonic Acid to Formic Acid.] *Chem. Ztg.*, vol. 39, 1915, pp. 72-73; *Chem. Abs.*, vol. 10, 1916, p. 1036.

Considerable amounts of free HCOOH are obtained by the action of H<sub>2</sub> and Pd black under pressure on CO<sub>2</sub> in the presence of H<sub>2</sub>O; the HCOOH is decomposed catalytically into CO<sub>2</sub> and H<sub>2</sub>. The determination of the equilibrium between these reactions between 30°-90° gave no indication of the formation of HCHO as an intermediate product, so that it is unlikely that the formation of the latter is a stage in the assimilation of CO<sub>2</sub> in nature.

340. BREDIG, G., AND SCHWANZ VON BERGKAMPF, E. [Hexagonal Nickel.] *Ztsch. physik. Chem., Bodenstein-Festband*, 1931, pp. 172-176; *Chem. Abs.*, vol. 26, 1932, p. 14.

Hexagonal Ni was prepared by the glow-discharge method of Bredig and Alolio in H<sub>2</sub>. With the Laue powder camera,  $a$  was found to equal 2.66 Å,  $c$  = 4.29 and  $c/a$  = 1.61. The theoretical value of  $c/a$

for hexagonal close packing is 1.63. In Ni, a material was obtained in which  $a$  = 2.60 Å,  $c$  = 4.15 and  $c/a$  = 1.60. The hexagonal Ni is nonmagnetic, but on heating to 300° it is transformed to magnetic Ni with a cubic lattice, in which  $a$  = 3.52 sq. Å.

341. BREMNER, J. G. M., AND BRADFORD, B. W. Oxo Synthesis. Interrogation of Dr. Roelen. *BIOS Interrogation Rept.* 737, January 1945, 5 pp.; *Bib. Sci. Ind. Rept.*, vol. 10, No. 2, 1948, p. 2; *PB* S1,965.

1. Bradford, B. W. 2. Dr. Roelen. 3. Oxo process. 4. Aldehydes production, Germany. 5. Alcohols production, Germany. 6. Detergents production, Germany. 7. I. G. Farbenindustrie A.-G., Leuna, Germany. 8. Fischer-Tropsch Plant, Courrières-Kuhlmann Oil, Harnes, France.

342. BRENDLEIN, —. Medium-Pressure Synthesis of Methanol. *FIAT Reel M-38*, frames S061-S074, 1942; frames S130-S132, 1943; *PB* 70,309.

Medium-pressure synthesis of MeOH takes place by way of methyl formate, which is isolated as such and then hydrogenated to MeOH. MeOH is converted into methyl formate with CO in the presence of sodium methyrate at a pressure of 30 atm. The methyl formate is reduced to MeOH on a catalyst of reduced Cu oxides. Higher alcohols can also be used as starting materials since their formates can be prepared and hydrogenated in the same way. Describes apparatus.

343. —. Synthesis of Methanol in Two Stages. *FIAT Reel M-38*, frames S130-S132, Mar. 22, 1943; *PB* 70,309.

Proposes process that makes it unnecessary to split the synthesis gas into CO and H<sub>2</sub>. After the synthesis gas is freed from CO<sub>2</sub> it is compressed at 30 atm., and the CO is rinsed out with a MeOH solution of sodium methyrate, which results in the formation of methyl formate. The residual gas, which still contains certain quantities of CO, is converted by steam and supplies enough H<sub>2</sub> for the reduction cleavage of the methyl formate.

344. —. Two-Stage Synthesis of Methanol. *FIAT Reel CC-140*, frames 1-51, September 1946; *PB* A70,207.

The 2 stages are:  $\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COOH} + 2\text{H}_2 \rightarrow 2\text{CH}_3\text{OH}$ . Catalyst for step 1 is sodium methyrate and for step 2 copper chromite. The process uses lower temperatures and pressures than the conventional method and eliminates side reactions. Drawings and flow sheets.

345. BRENNSTOFF-CHEMIE. [Japanese Seven-Year Plan.] *Wirtschaftsteil*, vol. 18, 1937, p. 39; *Coal Carbonisation*, vol. 3, 1937, p. 115.

Gives particulars of program under which motor-fuel requirements of Japan are to be met, mainly from domestic sources, by 1943. It is estimated that the requirements of light fuels, mainly gasoline, will then amount to about 545 million gal. per yr., 335 million gal. of which is to be supplied by home production. About 630 million gal. of heavy oils will be needed, and about half of this amount is to be produced from domestic materials. Plan is based on producing 132 million gal. of light fuels and 93 million gal. of heavy oil from coal and 86 million gal. of light oils and 46 million gal. of heavy oils by synthesis. A German firm has been entrusted with the planning of a plant for the synthesis of 33,000 tons of gasoline per yr. by the Fischer-Tropsch process. Low-temperature carbonization of coal is to yield about 9 million gal. of light motor fuels and 112 million gal. of heavy oils, requiring about 9 million tons of coal. The remainder of the liquid-fuel output is to be in the form of potato spirit and the refined products of domestic oils. It is

estimated that the capital investment will be about 750 million yen apart from 127 million yen to be spent on increasing the coal output.

346. —. [Dismantling of the Fischer-Tropsch and Gelsenberg Synthetic Fuel Plants.] *Wirtschaftsteil*, vol. 30, No. 11-12, 1949, pp. 29-31.

Gives German viewpoint concerning the dismantling of the synthetic-fuel plants in western Germany. Preservation and operation of the plants are economically of great significance, in that several thousand men would be employed in producing domestic-fuel and primary-chemical products. The 6 Fischer-Tropsch plants have a capacity for producing 370,000 tons of primary products annually, and the Gelsenberg coal-hydrogenation plant has a capacity for processing about 1,000,000 tons of crude oil or 540,000 tons of heavy-residual oils.

347. —. [Status of Krupp Treibstoffwerk G. m. b. H. Operation.] *Wirtschaftsteil*, vol. 31, 1950, p. 41.

It is known that at the end of last year permission had been withdrawn by the Allied High Commission from the Krupp Treibstoffwerk to produce hydrocarbons by the Fischer-Tropsch process. Since that time permission has been granted to operate the Oxy process, which has been developed by the Ruhrchemie A.-G. According to this new process valuable products, designated higher alcohols, can be produced. These products will be processed into a number of other products, which will not only be of considerable importance domestically but will also be valuable for export. Among the products are mentioned solvents for the paint and dye industries and softeners for plastics and detergents. It is the intention of both Krupp and Ruhrchemie A.-G. to work together in putting out these Oxy products. Ruhrchemie A.-G. will make the necessary catalysts in its own catalyst factory.

348. BRETEAU, Hydrogenations in Gaseous System. *Catalysis in Organic Chemistry*, P. Sabatier, D. Van Nostrand Co., New York, 1922, p. 186.

CO can be reduced in the cold, or better at 400°, to CH<sub>4</sub> in the presence of Pd sponge.

BREWER, R. E. See abs. 920, 929.

349. BREYTWISCH, —. [Synol Synthesis.] *Scientific Contribution No. 10* from the Laboratory of the Merseberg Ammonia Plant, April 1943, 2 pp.; *PB* S69.

It was discovered at Leuna that the medium-pressure synthesis for the production of hydrocarbons by the reduction of CO could be directed so that up to 60% of the product would consist of unbranched aliphatic alcohols. A catalyst similar to the Leuna NiH<sub>2</sub> catalyst, in which the K content was 0.1-0.7% and which had been reduced in an excess of H<sub>2</sub> (1:1000) at 400°-500°, was used. The conversion of CO and H<sub>2</sub> amounted to 1:150 or 25% more than in technical benzene synthesis at 190°-200°. The pressure should be above 20 atm., preferably 25 atm. The yield of primary product was 0.4-0.5 ton/m.<sup>3</sup> of catalyst/day. The CO and H<sub>2</sub> were in the ratio of 1:1, and the synthesis was performed in 3-4 successive steps. Both H<sub>2</sub>O and CO<sub>2</sub> were obtained as byproducts instead of only H<sub>2</sub>O as with Co catalyst. With the Fe catalyst, a gas ratio of nearly 2H<sub>2</sub>:CO could be maintained by recycling the gas so rapidly over the catalyst that the partial pressure of the water vapor, which underwent conversion with the CO, remained low. The synthesis products must be removed quickly from contact with the catalyst in order to avoid secondary reactions such as dehydration and hydrogenation. The primary products with small amounts of acids, aldehydes, 15% of gasol, and 5-10% of CH<sub>4</sub> were as follows:

	Percent	Alcohol	Olefins	Esters
Up to 200°	50	50	20	2
200°-230°	3	60	22	8
230°-250°	17	65	25	8
250°-300°	3	50	30	10
350°-400°	12			
Above 400°				

Increase in pressure, CO content, and K content of the catalyst increased the yield of paraffins, whereas decrease in pressure, CO content, and K content as well as an increase in conversion increased the formation of gasol. Some directions are given for recovering and working up the products, and some possible uses for the various fractions are mentioned.

350. BRIDGEWATER, R. M. British Research on Petroleum Substitutes. VI. Fischer-Tropsch Synthesis. Petroleum (London), vol. 8, 1945, pp. 109-111; Jour. Inst. Petrol., vol. 31, 1945, p. 320 A.

Although 7 million gal. of MeOH were produced in Britain in 1 yr. before the war by the interaction of CO and H<sub>2</sub> and about 600,000 tons of oil/yr. by Fischer-Tropsch process in Germany by 9 plants, little experimental work appears to have been carried out in Britain. British work concerned the development of robust catalysts and techniques for large-scale operation. Synthetic Oils, Ltd., worked on a process yielding a product rich in olefins, using specially prepared catalysts. A plant was built to process about 200,000 cu. ft. of gas/day, yielding 136-180 gal./day, and said to substantiate the results obtained in the pilot plant using blue water gas. With Co and Th carbonates supported on kieselguhr, the Fuel Research Station produced lubricating oils from blue water gas and H<sub>2</sub> in a small plant. Little has been reported on the quality of motor spirit or Diesel oils produced, but a fraction boiling 210°-300° C. has a cetene number of 93. The 7-10% wax contained in liquid products from Fischer-Tropsch process can be treated to yield marketable commodities. Studies have been made of the mechanism of the process, it being concluded that Co carbide is first formed.

351. ———. British Research on Petroleum Substitutes. VII. Synthetic Lubricating Oils. Petroleum (London), vol. 8, 1945, pp. 130, 152-153.

First gives some consideration to the existing knowledge concerning the composition and the chemical and physical properties of lubricating oils derived from petroleum. The absence of real knowledge as to the physical and chemical properties required in a lubricating oil has been a major difficulty in researches on synthetic lubricating oils. The various raw materials available for the manufacture of synthetic lubricating oils are: Coal-carbonization products, including tar fractions and C<sub>2</sub>H<sub>4</sub>; products of the pressure hydrogenation of coal or tar; and the primary products of the Fischer-Tropsch process. The principal methods for producing lubricating oils from these products are: Isolation of suitable fractions by distillation or solvent extraction; stabilization of such fractions by hydrogenation; polymerization of hydrocarbons, especially olefins, with or without catalysts; chlorination of hydrocarbons, especially high-boiling paraffins, followed by dechlorination; condensation of chlorinated hydrocarbons or olefins with aromatic hydrocarbons. Lubricating oils from the neutral-oil fractions of low-temperature tar were unsatisfactory, even after hydrogenation over a Mo catalyst. The viscosity was too low at the higher temperatures, and there was too great a tendency toward oxidation and carbonization. Better results might be attained by using the superior hydrogenation catalysts subsequently discovered.

352. BRIDGMAN, P. W. Recent Work in the Field of High Pressures. Rev. Modern Phys., vol. 18, 1946, p. 1-93; Jour. Inst. Petrol., vol. 32, 1946, p. 254 A.

Summarizes work on high pressures from 1930, the date of publication of Bridgman's book, The Physics of High Pressure, to June 1945, with 674 literature references. The high-pressure range now open to study extends to 100,000 atm. The effects of high pressures on chemical reactions in liquid and vapor phases, both catalyzed and uncatalyzed, are reviewed. Reactions listed include the pyrolysis, hydrogenation, oxidation, and polymerization of hydrocarbons. The majority of the chemical studies discussed are of direct industrial interest.

353. BRILL, —. Behavior of Calcium in the Ammonia Catalyst Toward Poisoning. FIAT Reel R-19, frames 7088-7104, 1941.

Test results on Fe catalysts containing Ca for the NH<sub>3</sub> synthesis proved that an addition of Ca in combination with the usual addition of Al has several advantages. Above all, the resistance of the catalyst to poisoning by CH<sub>4</sub> and H<sub>2</sub>S is increased. Tabular data present further details. A number of catalysts with and without Ca are arranged according to the degree of their sensitivity to H<sub>2</sub>S, H<sub>2</sub>P, CH<sub>4</sub>, and O.

354. BRILL, R. [X-Ray Investigation of the Iron Carbonyl, Fe(CO)<sub>5</sub>.] Ztschr. Krist., vol. 65, 1927, pp. 85-93; Chem. Abs., vol. 21, 1927, p. 3775.

Fe<sub>2</sub>(CO)<sub>9</sub> is hexagonal with a unit cell of the dimensions  $a = 6.45$  and  $c = 15.8$  Å. U., which contains 4 mol. The space group may be C<sub>2</sub>h, C<sub>2</sub>h, D<sub>2</sub>h, or D<sub>3</sub>h. The 9 CO groups are at the corners of 2 octahedrons with a common face. The Fe atoms are on the trigonal axis perpendicular to this common face.

355. BRILL, R., AND MARK, H. [Röntgenographische Studien on the Structure of Complex Iron Cyanides.] Ztschr. physik. Chem., vol. 133, 1928, pp. 443-445; Chem. Abs., vol. 22, 1928, p. 3073.

(NH<sub>4</sub>)<sub>2</sub>[Fe(CN)<sub>5</sub>] and S of the substances resulting from its stepwise reduction at 400° with time were subjected to diffraction analysis. 3 crystalline phases were found, and in some cases many more. Besides the initial compound and the final α-Fe, another compound certainly was (Fe(CN)<sub>5</sub>)<sub>2</sub>, cubic,  $d_{100} = 15.9$  Å. U., molecular formula (Fe(CN)<sub>5</sub>)<sub>2</sub> = Fe<sub>2</sub>[Fe(CN)<sub>5</sub>]<sub>2</sub>. Hence the reduction mechanism must be: (NH<sub>4</sub>)<sub>2</sub>[Fe(CN)<sub>5</sub>] → α-Fe. The supposition is made that the appearance of certain extra lines in the diffraction pattern of the product obtained when H<sub>2</sub> and N<sub>2</sub> act on ammonium ferrocyanide at 400° is due to a carbide of unknown structure.

355a. BRIMM, E. O. AND LYON, M. A. Estimated Bond Order in Metal Carbonyls. Am. Chem. Soc. 121st Meeting Abs., March-April, 1952, p. 38-N.

The presence of partial double bond character of the metal-C bond in metal carbonyls has been postulated to account for the shortness of the observed bond lengths. The % double bond character of the metal-C bonds in metal carbonyls, substituted metal carbonyls and hydrocarbons is estimated by means of Pauling's principle of electroneutrality. A decrease in the order of the C-O bond would result from this partial double bond formation. Changes in the characteristic infrared absorption of the C-O bond are correlated with the estimated bond orders. Evidence is presented for the presence of bridging CO in dicobalt octacarbonyl and tetracobalt dodecacarbonyl and their absence in dimanganese dodecacarbonyl and dirhenium dodecacarbonyl.

356. BRINER, E., AND SENGLET, R. [Experiments on the Carbides of Aluminum, Nickel, and Copper.] Jour. chim. phys., vol. 13, 1915, pp. 351-375; Chem. Abs., vol. 10, 1916, p. 3041.

On being heated Al<sub>2</sub>C<sub>3</sub> dissociates into its elements, which in the presence of air are immediately oxidized. The reaction was studied at 540°, but the decomposition is appreciable at lower temperatures. In the synthesis of the substance, powdered Al was heated with sugar C for 2-hr. periods and the residue tested for presence of carbide by the addition of HCl to produce CH<sub>4</sub>. At 550° no appreciable quantity was formed, but at 750° and 900°, respectively, small fields were obtained, proving the reaction of Al<sub>2</sub>C<sub>3</sub> = 4Al + 3C to be reversible. Attempts to measure the speed of the reaction were unsuccessful. Ni<sub>2</sub>C is formed according to the equation 3Ni + C = Ni<sub>2</sub>C at temperatures about 2,100°; at lower temperatures it dissociates into its constituents, rapidly at 1,600° and relatively slowly at 900°. At the relatively low temperatures, while the interacting substances are in the solid state, the reaction is endothermic; at the higher temperatures, when the Ni and C are gaseous and in the atomic state, it becomes exothermic. Studies of the formation of carbides of Cu indicate that an endothermic carbide is formed at high temperatures that decomposes at 1,600°, but further confirmatory work is needed.

357. BRINKLEY, S. R. Calculation of Catalyst and Gas Temperatures in Adiabatic Contact Catalytic Reactions. Am. Chem. Soc. 110th Meeting Abs., Div. Ind. Eng. Chem., 1946, p. 42 I.

Temperatures of catalyst and gas in contact-catalytic reactions is computed on the assumptions that all but a negligible amount of the heat of reaction is removed by means of the sensible heat of the gas stream and that the overall conversion of reactants to products is limited by means of small contact time to a few % of the total gas. At constant velocity, the temperatures of catalyst and gas are found to increase exponentially with increase in depth of catalyst bed. The yield is proportional to the overall temperature rise of the gas stream. The effect of change in velocity on the temperature of the catalyst is investigated by the assumption that the coefficient of heat transfer from catalyst to gas is proportional to the 0.7 power of the velocity. The temperature of catalyst and gas are estimated for a typical German operation of the Michael hot-gas recycle process for the middle-pressure synthesis of hydrocarbons from CO and H<sub>2</sub> on an Fe catalyst. On the basis of approximate data, it is estimated that the catalyst temperature is between 7° and 9° higher than the gas temperature for a half-meter catalyst bed, flow rate 1 m./sec., and overall gas temperature rise of 10°.

358. ———. Heat Transfer Between a Fluid and a Porous Solid Generating Heat. Jour. Appl. Phys., vol. 18, 1947, pp. 582-585; Chem. Abs., vol. 41, 1947, p. 5007.

The theory, due to Anzelius, of the transfer of heat between a fluid flowing with constant velocity through a porous solid is extended to include the case where the solid generates heat. Expressions are obtained for the temperatures of solids and fluid as functions of position and time, it being assumed that the heat source function is a linear function of the temperature of the solid with coefficients independent of position and time. The application of the theory to the calculation of catalyst and gas temperatures in a typical operation of the Michael process for the synthesis of hydrocarbons from CO and H<sub>2</sub> is indicated.

359. ———. Contact Times of Continuous-Flow Reacting Systems With Volume Change. Ind. Eng. Chem., vol. 40, 1948, pp. 303-307; Chem. Abs., vol. 42, 1948, p. 2849.

General relation between contact time and space velocity is obtained by comparing the solutions of the Euler and Lagrange forms of the hydrodynamical steady-state equations for the composition of a flowing system that undergoes chemical reaction with accom-

panying volume change. It is assumed that the reactor is isothermal and isobaric and that the flow is 1-dimensional. This relation is applied to the calculation of contact times for particular rate laws. An approximate formula is developed for estimation of contact times when the rate law is unknown, and the resulting error is obtained for several cases by a direct numerical comparison with the correct expressions. These considerations apply to catalytic reactions on granular catalysts if apparent contact time is calculated from a space velocity defined as the volume of gas at the temperature and pressure of the feed gas/free vol. of the catalyst bed/unit of time.

360. BRISKINA, A. I., AND MOGLEVSKAYA, A. M. [Gasification of the Donets Anthracites to Produce Water Gas and Mixed Gas.] Khim. Tverdogo Topliva, vol. 8, 1937, pp. 1165-1181; Chem. Abs., vol. 32, 1938, p. 4809.

Under optimal conditions (the intensity of air blowing about 26,350 m<sup>3</sup>/hr., that of steam blowing 5,896 kgm./hr., the air pressure under the grating 1,204 mm., and the height of the fuel layer 1,900 mm.) the water gas contained CO, 6.74%, H<sub>2</sub>S, 0.43%, O<sub>2</sub>, 0.20%, CO 39.23%, H<sub>2</sub>, 47.03%, CH<sub>4</sub>, 0.51%, and N<sub>2</sub>, 5.57% by volume and had a calorific value of 2,700-2,455 cal./m<sup>3</sup>. The air gas contained CO, 14.29%, H<sub>2</sub>S, 0.08%, O<sub>2</sub>, 0.17%, CO, 9.51%, H<sub>2</sub>, 2.45%, CH<sub>4</sub>, 0.15%, and N<sub>2</sub>, 73.63%; its calorific value was 382-369 cal./m<sup>3</sup>. Gasification for production of a mixed gas yielded CO, 7.42%, H<sub>2</sub>S, 0.19%, O<sub>2</sub>, 0.17%, CO, 24.99%, H<sub>2</sub>, 15.19%, and N<sub>2</sub>, 0.30%, of calorific value 1,262-1,185 cal./m<sup>3</sup>.

361. BURROW, W. A. Oil From Coal. Engineer, vol. 168, 1939, pp. 469-470; Gas Jour., vol. 228, 1939, pp. 288-290; Colliery Guard., vol. 159, 1939, pp. 625-626; Engineering, vol. 148, 1939, pp. 361-362.

Not only, as at present, can the Fischer synthesis be used to produce liquid fuels, certain fractions of which are rich in olefins useful for the manufacture of lubricating oils and paraffins subject to oxidation into fatty acids, but also it will be only a question of time and research until gases will be produced that are rich enough in mono-olefins to be polymerized into high-octane gasolines. Another revolution will be accomplished if conversion of CH<sub>4</sub> and its homologs into olefins can be carried out commercially. This is important to both the oil and the coal industries—to the former because of the immense quantities of CH<sub>4</sub> contained in natural gas and to the latter because of the high % of CH<sub>4</sub> in coke-oven gases.

362. ———. Fuel and Allied Industries. Gas and Oil Power, vol. 35, 1940, pp. 236-237; Chem. Abs., vol. 35, 1941, p. 875.

Lecture with emphasis on synthesis of hydrocarbons.

363. ———. Coal and Oil—Survey of New Facts and Future Possibilities. Gas World, vol. 118, No. 3065, coking sec., 1943, pp. 60-63; Chem. Abs., vol. 37, 1943, p. 3904.

An address. The blending of synthetic diesel fuel produced by the Fischer-Tropsch process with an equal quantity of the diesel fractions of the oils from high-temperature carbonization to give a suitable diesel fuel is suggested.

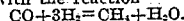
364. BROCHE, H. [Liquid Fuels From Coal in Relation to German Power Economics.] Glückauf, vol. 70, 1934, pp. 1137-1149; Chem. Abs., vol. 29, 1935, p. 4151.

Lacking petroleum, Germany must procure liquid fuels for future transport development largely from coal. Liquid fuels by carbonization can be increased by (a) mild refining of coke-oven light oils; (b) use of the roof-canal and the Still process for protecting coke-oven light oils from decomposition; (c) further development of low-temperature carbonization. Hydrogenation and synthesis from water gas will become

important sources of liquid fuels. Some progress has been made in the adaptation of the diesel motor to tar oils by use of a special fuel injector.

365. BRODIE, B. C. Synthesis of Methane and Formic Acid. Proc. Roy. Soc., vol. 21, 1872, pp. 245-247; Jour. Chem. Soc., 1873, p. 744; Chem. News., vol. 27, 1872, p. 187; Chem. Zentralbl., 1873, p. 451.

On passing an electric current through a mixture of CO and H<sub>2</sub>, after 5 hr. about 6% of CH<sub>4</sub> was detected in accordance with the reaction



In a corresponding test with a mixture of CO<sub>2</sub> and H<sub>2</sub>, the resultant gas was found to contain, besides H<sub>2</sub> and unchanged CO<sub>2</sub>, some CO and CH<sub>4</sub> and an oily liquid identified as HCOOH.

366. ———. Formaldehyde Synthesis. Proc. Roy. Soc., vol. 22, 1873, p. 172.

CH<sub>2</sub>O is produced when the silent electric discharge is passed through a mixture of CO<sub>2</sub> and H<sub>2</sub>.

367. ———. Formaldehyde Synthesis. Angew. Chem., vol. 174, 1874, p. 284.

On passing an electric current through a mixture of CO<sub>2</sub> and H<sub>2</sub>, about 5.2% of HCHO was detected in the end gas, and with CO and H<sub>2</sub>, only CH<sub>4</sub> and CO<sub>2</sub> were obtained.

368. BRODIE, G. H., JENNINGS, W. H., AND HAYES, A. Heat of Formation of Cementite as Electrolyzed From a Pure Iron-Carbon Alloy of Eutectoid Structure and Composition. Trans. Am. Soc. Steel Treating, vol. 10, 1926, pp. 615-629; Chem. Abs., vol. 21, 1927, p. 3878.

Value of -13,580 cal. per gm. mol. was obtained at 86° F. by calorimetric determination of the heat of formation of Fe<sub>3</sub>C.

BRODIE, F. See abs. 1786, 1787.

369. BROETZ, W. [Systematics of the Fischer-Tropsch Catalysts.] Ztschr. Elektrochem., vol. 53, 1949, pp. 301-306; Chem. Zentralbl., 1950, I, p. 1432; Chem. Abs., vol. 44, 1950, p. 2858.

Fundamental Fischer-Tropsch reaction:  $\text{CO} + 2\text{H}_2 > \text{CH}_3 + \text{H}_2\text{O}$  at atmospheric and at 5-20 atm. gage pressure between 160° and 186° is discussed. On technical catalysts at pressures up to 10 atm. gage pressure the reaction rate is given by:  $d[\text{CO}]/dt = k_1 [\text{H}_2]^2 / [\text{CO}]$  where  $k_1$  at 7 atm. gage pressure varies from  $7.8 \times 10^{-3}$  at 173° to  $1.88 \times 10^{-2}$  at 180°, yielding an activation energy of 31 kcal. per mol. At atmospheric pressure an activation energy of 28 kcal. per mol. is found. At high pressures the reaction rate is:  $d[\text{CO}]/dt = \frac{k_2}{k_3} [\text{H}_2]^{1.5} [\text{CO}]^{0.5} (1 + k_4 [\text{H}_2])^{-1}$ . The presence of CH<sub>4</sub> in the reaction mixture does not affect the rate or the nature of the products. The catalysts gradually lose activity, which may be recovered by heating in H<sub>2</sub> at 400°. The reaction takes place directly in 1 step at the catalyst surface without formation of an intermediate carbide. The CH<sub>3</sub> radicals are combined at the catalyst surface under formation of double bonds at the chain ends, which are subsequently shifted by H exchange toward the center of the chains.

370. BROETZ, W., AND SPENGLER, H. [Physicochemical Behavior of Fischer-Tropsch Catalysts.] Brennstoff-Chem., vol. 31, 1950, pp. 97-102; Chem. Abs., vol. 44, 1950, p. 6240.

Conversion behavior of a porous catalyst depends not only on its special chemical properties but also on the structure of its pore system, which makes up its inner surface and provides the path for the transport of the reactants. The following determinations were made for the purpose of clarifying the pore structure of Fischer-Tropsch catalysts: (1) Determination of the grain and lattice volumes of unreduced

catalysts. From the data thus obtained the pore volumes and the porosity as well as the change in volume through reduction of the catalyst are determined. (2) Plotting a structure curve in order to find out how the micropore space is divided among the various pore radii. (3) Determination of the average pore radius of the macropores by means of a perfusion method. By this means there results for CO and H<sub>2</sub> an excess flow, which is designated as surface diffusion and explains the otherwise determined complete utilization of the catalyst grain. (4) Determination of the inner surface by plotting an adsorption isotherm. In connection with surface determination, absorption measurements of CO and H<sub>2</sub> show that the temperature region of Fischer-Tropsch synthesis corresponds to the beginning chemisorption of this gas. The heat of adsorption of CO and H<sub>2</sub> is calculated from the adsorption isotherms. (See abs. 3243.)

371. BROXI, N. [The Motor-Fuel Crisis and Remedies for Surmounting It.] Giorn. bibliografia tecnica intern., 1925, No. 2, pp. 1-8, Nos. 3-4, pp. 3-13, No. 5, pp. 1-8, No. 6, pp. 1-9; 1926, No. 1, pp. 3-9; Chem. Abs., vol. 20, 1926, p. 1898.

Extended review and discussion dealing with different types of motor fuels, general methods available for increasing their supply, methods of increasing the yield of benzene from crude oils, the recovery of benzene from solid, liquid, and gaseous substances, the liquefaction of natural gas, distillation of coals, lignites, and peat, production of artificial petroleum by direct synthesis and from vegetable and animal oils, and the direct use of vegetable oils, alcohol, gas-producer gas, and colloidal mixtures as fuels. Includes economic as well as chemical and engineering data.

BROOKS, A. P. See abs. 2064.

BROUGHTON, J. W. See abs. 298.

372. BROWN, B. K., AND GUNNESS, R. C. Future Fuels—Liquid and Gaseous. Mech. Eng., vol. 70, No. 5, 1948, pp. 421-424; Chem. Eng. News, vol. 26, 1947, pp. 2128-2127, 2171; Chem. Abs., vol. 42, 1948, p. 4323 (Brown and Gunness), p. 6509 (Gunness).

Demand for petroleum products has quadrupled during the last 25 yr., and it may be expected to increase another 30% by 1970, at which time the total demand will exceed 7 million bbl. per day. This demand will be met by domestic crude-oil production, some foreign imports, and by synthesis from natural gas and coal. Oil from shale and tar sands seems to be more remote than from synthesis. The economics of the industry will result in a gradually diminishing supply of residual fuel oil for industrial purposes, and coal will handle an increasing share of the expanding industrial fuel load. This means a very large future development in coal mining to take care of the increasing demand for coal. To produce even 1 million bbl. of oil per day from coal will require the mining and processing of 650,000 tons of coal per day or 236 million tons per yr., or nearly one-half of our present production.

BROWN, E. A. See abs. 3551.

BROWN, G. G. See abs. 1121.

BROWN, R. L. See abs. 921, 922, 928.

373. BROWN, R. L., AND GALLOWAY, A. E. Methanol From Hydrogen and Carbon Monoxide. I. Ind. Eng. Chem., vol. 20, 1928, pp. 960-966; Fuel, vol. 47, 1928, pp. 518-525; Chem. Abs., vol. 22, 1928, p. 4104.

Experimental production of MeOH from H<sub>2</sub> and CO has been studied, with ZnO, basic ZnCrO<sub>4</sub>, and normal ZnCrO<sub>4</sub> as catalysts. The last 2 are more active than ZnO, and under high-temperatures and pressures the normal ZnCrO<sub>4</sub> is the most active. With the theoretical mixture of CO and H<sub>2</sub> at 400° and 180 atm., a 20% conversion of CO to MeOH has been obtained.

374. ———. Methanol From Hydrogen and Carbon Monoxide. II. Dimethyl Ether. Ind. Eng. Chem., vol. 21, 1929, pp. 310-313; Chem. Abs., vol. 23, 1929, p. 2150.

Production of Me<sub>2</sub>O (I) as a side reaction of the synthesis of MeOH (II) over ZnCrO<sub>4</sub> at 300°-400° and 180 atm. has been studied. The formation of I is slow and increases with temperature to 5.2% at 397° while II reaches a maximum of about 30% at 375° and then falls off. High space velocity favors formation of II.

375. ———. Methanol From Hydrogen and Carbon Monoxide. III. Further Work on Dimethyl Ether. Ind. Eng. Chem., vol. 22, 1930, pp. 175-176; Chem. Abs., vol. 24, 1930, p. 1840.

Catalyst prepared by precipitating the nitrates with NaOH to give an atomic ratio of 3 Cu : 1 Cr in contact with a 2 : 1 H<sub>2</sub> : CO mixture at 180 atm. yielded MeOH and Me<sub>2</sub>O in the following molecular % ratios: 265°: 7 : 4; 285°: 14 : 6; 305°: 24 : 22; 340°: 17 : 20; 355°: 11.5 : 13.5. The region of maximum conversion was 315°-320°, and conversions were on the order of 30 mol. %, that to Me<sub>2</sub>O being the larger.

BROWNE, R. Y. See abs. 576.

BROWNING, L. C. See abs. 2008.

376. BROWNING, L. C., AND EMMETT, P. H. Equilibrium Measurements in the System C-CH<sub>4</sub>-H<sub>2</sub>. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 581-583; Chem. Abs., vol. 45, 1951, p. 4534.

In the course of experiments relative to the Fe-Fe<sub>3</sub>C-CH<sub>4</sub>-H<sub>2</sub> equilibria, it was found that the C formed by the decomposition of Fe<sub>3</sub>C reacted readily with H<sub>2</sub> at temperatures as low as 400°, the Fe catalyzing the reaction. A study was made of the CH<sub>4</sub>-C+2 H<sub>2</sub> equilibrium constants in the temperature range 350°-535°, using the C formed as above. The values obtained are close to those for the reaction in which the C-form is β-graphite.

377. BROWNING, L. C., DEWITT, T. W., AND EMMETT, P. H. Equilibria in the Systems Fe<sub>3</sub>C-Fe-CH<sub>4</sub>-H<sub>2</sub> and Fe<sub>3</sub>C-Fe-CH<sub>4</sub>-H<sub>2</sub>. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 4211-4217; Chem. Abs., vol. 45, 1951, p. 1861.

Equilibrium constants for the reaction (I) CH<sub>4</sub>+2 Fe<sub>3</sub>C=Fe<sub>3</sub>C+2H<sub>2</sub> were reported in the temperature range 295°-350° and for the reaction (II) CH<sub>4</sub>+3 Fe<sub>3</sub>C=Fe<sub>3</sub>C(β)+2H<sub>2</sub> in the temperature range 320°-468°. Free energies of formation of Fe<sub>3</sub>C and Fe<sub>3</sub>C<sub>2</sub>, calculated from the data for reactions (I) and (II), led to the conclusion that the formation of all mono-olefins and of saturated hydrocarbons containing more than 6 C atoms by the direct reduction of Fe<sub>3</sub>C and Fe<sub>3</sub>C<sub>2</sub> in the temperature range 450°-650° K. is thermodynamically unfavorable. The results obtained for reaction (II) agree well with those obtained at higher temperatures by Watase (abs. 3616).

378. BROWNIE, D. Australian Viewpoint on Oil Production From Coal. Iron and Coal Trades Rev., vol. 136, 1938, pp. 653-654.

Summary of a report prepared for the Minister in Charge of Australian Commonwealth Council for Scientific and Industrial Research by Sir D. Rivett. The conclusion is against recommending that any public money be provided at the present time for so costly a project. The study covered low-temperature distillation, hydrogenation of coal, and synthesis of hydrocarbons from CO and H<sub>2</sub>.

379. ———. Oil-From-Coal Developments. Coal and Colliery News, No. 2408, May 4, 1939, pp. 420-421.

Fischer-Tropsch process has not developed in Great Britain. Synthesis-gas products are known to have inferior antiknock qualities, and it is necessary to blend with benzol or add tetraethyl lead. Reports from the Robinson-Bindley synthetic-oil plant show Ni

catalysts on carriers employing silicic acid to be highly resistant to S poisoning.

380. BRÜCHANOV, A. [Effect of Compressive Stress on Disintegration of Cementite.] Ztschr. anorg. Chem., vol. 218, 1934, pp. 146-150; Metallurgia, vol. 9, No. 5, 1934, pp. 37-40; Chem. Abs., vol. 28, 1934, p. 5792.

Experiments with cast bars consisting of pearlite and cementite showed that cementite was stable up to temperatures of about 500°, but under pressure it begins to disintegrate at that temperature and disintegrates more with higher pressures. As the stability of cementite decreases with increasing temperature, the effect of pressure becomes less appreciable at higher temperatures and cannot be observed above 750°.

381. BRÜCKNER, H. [Coke-Oven Gas as a Chemical Raw Material.] Ztschr. Ver. deut. Ing., vol. 75, 1931, pp. 93-97; Chem. Abs., vol. 25, 1931, p. 3806.

Availability, generation, and utilization of coke-oven gas are considered from an economic viewpoint. Separation of 10<sup>6</sup> cu. m. of gas of average composition into its components should furnish 49,000 tons CO<sub>2</sub>, 23 tons C<sub>2</sub>H<sub>4</sub>, and homologs, 14 tons C<sub>2</sub>H<sub>6</sub>, 70 tons CO, 47 tons H<sub>2</sub>, and 178 tons CH<sub>4</sub>. Coal hydrogenation, synthesis of fuel oils, of NH<sub>3</sub>, MeOH, and of well-known C<sub>2</sub>H<sub>4</sub> derivatives are now technically perfected, and offer promising outlets, but only for very large scale operation.

382. ———. [Brown Coal and Peat-Gas Syntheses.] Handbuch der Gasindustrie, vol. 2, pt. 2, 1940, SS pp.; TOM Reel 241.

383. ———. [Formation of Methane From Carbon Monoxide-Hydrogen Mixtures in Contact With Low-Temperature Coke at Increased Pressures.] Brennstoff-Chem., vol. 20, 1939, pp. 346-348; Chem. Abs., vol. 34, 1940, p. 7582.

Conversion of H<sub>2</sub> into CH<sub>4</sub> in presence of low-temperature coke (5 gm. of coke, 1 liter of H<sub>2</sub>, standard conditions per hr., 50 atm.) rose from 7% at 500° to 23% at 700°. Correspondingly lower values were obtained at lower pressures. CH<sub>4</sub> was also formed when a water gas was similarly treated; the reaction in this case, however, was principally 2CO+2H<sub>2</sub>=CH<sub>4</sub>+CO. The maximum yield of CH<sub>4</sub>, 40% in the outlet gas, was obtained at 40 atm. and 700°; the yield fell with rising pressures.

See abs. 408.

385. BRÜCKNER, H., AND CHOLLAT, G. [Utility of Residual Gas From the Fischer-Tropsch-Ruhrchemie Process as City Gas.] Gas- u. Wasserfach, vol. 83, 1940, pp. 497-499; Chem. Abs., vol. 35, 1941, p. 300.

Analyses of the residual gas from the gasoline plant showed the following variations and average values over a period of 18 days: CO, 13.5-19.8%, ave. 17.0%; unsaturated 0.3-1.1%, ave. 0.7%; O<sub>2</sub>, 0.0-0.2%, ave. 0.1%; CO<sub>2</sub>, 2.9-11.9%, ave. 9.0%; H<sub>2</sub>, 11.3-23.6%, ave. 20.0%; CH<sub>4</sub>, 27.6-40.9%, ave. 33.0%; N<sub>2</sub>, 16.5-35.1%, ave. 20.2%. The average gross heating value was 4,170 kg.-cal. per m.<sup>3</sup> (0°, 760 mm. Hg. and dry) and average density 0.755. The maximum rate of flame propagation was 29 cm. per sec. as compared with 70-95 cm. per sec. for manufactured gas. The highest specific-flame intensity (combustion density) was approximately 740×10<sup>-4</sup> kg.-cal. per cm.<sup>2</sup> per sec. as compared with about 1,200 for manufactured gas. These last two characteristics make the gas unsuitable for use alone as city gas, but a maximum of 25-30% can be mixed with coke-oven gas.

385. BRÜCKNER, H., AND JACOBUS, G. [Activity of Nickel Catalysts for the Synthesis of Methane.] Brennstoff-Chem., vol. 14, 1933, pp. 265-268; British



Chem. Abs., B, 1933, p. 772; Chem. Abs., vol. 27, 1933, p. 5154.

Addition of SiO<sub>2</sub> gel, Al<sub>2</sub>O<sub>3</sub>, ThO<sub>2</sub>, or the oxides of Ba, Sr, and Ca activates or increases, in the order named, the life of Ni catalysts. The weekly alkaline catalysts of pure Ni, Ni-alkaline earths, and Ni-ThO<sub>2</sub>, prepared by reducing the hydroxides, are almost completely inactive. The Ni-Al<sub>2</sub>O<sub>3</sub> catalyst, however, is highly active, yet when prepared by calcining the nitrate it is inactive. On the other hand, nitrate-prepared Ni, Ni-alkaline earths, and Ni-ThO<sub>2</sub> are active. The best catalysts are mixtures of 90% Ni and 10% Al<sub>2</sub>O<sub>3</sub> or ThO<sub>2</sub>. Additions of alkaline earths, particularly of BaO, increase many times the activity of the catalysts prepared from the nitrate. Addition of Co greatly decreases the activity of Ni, while Cu makes it completely inactive. Reviews literature briefly.

BRUDE, G. See abs. 900, 901.

BRUNAUER, S. See abs. 822, 823, 824, 825, 826, 827, 836, 2215, 2216.

386. BRUNAUER, S., AND EMMETT, P. H. Use of van der Waals' Adsorption Isotherms in Determining the Surface Area of Iron-Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 57, 1935, pp. 1754-1755; Chem. Abs., vol. 29, 1935, p. 7168.

The determination of van der Waals' adsorption isotherms of gases close to their boiling points affords a convenient method of measuring the extent of surface of Fe-synthetic-NH<sub>3</sub> catalysts; low-temperature isotherms are given for N<sub>2</sub> at -195.8° and -183° for O<sub>2</sub>, CO, and A at -183°, for CO<sub>2</sub> at -78.5°, and for C<sub>2</sub>H<sub>6</sub> at 0°.

387. ———. Use of Low-Temperature van der Waals' Adsorption Isotherms in Determining the Surface Areas of Various Adsorbents. Jour. Am. Chem. Soc., vol. 59, 1937, pp. 2682-2689; Chem. Abs., vol. 32, 1938, p. 1159.

Van der Waals' adsorption isotherms of some or all of the following gases were determined on a variety of adsorbents at the temperatures indicated: A and N<sub>2</sub> at -195.8°; A, N<sub>2</sub>, CO, and O<sub>2</sub> at -183°; CO<sub>2</sub> at -78°; normal C<sub>2</sub>H<sub>6</sub> and SO<sub>2</sub> at 0°. The following adsorbents were used: 2 Cu catalysts, glaucosil, pumice, NiO supported on pumice, Ni on pumice, dry powdered bacteria, Cr<sub>2</sub>O<sub>3</sub> gel, "glowed" Cr<sub>2</sub>O<sub>3</sub>, KCl, CuSO<sub>4</sub>·5H<sub>2</sub>O, CuSO<sub>4</sub>, 2 SiO<sub>2</sub> gel samples, activated charcoal, and 2 Darco samples (activated carbons). All adsorbents except charcoal given sigmoid isotherms, and the values for the surface area evaluated from the different isotherms for the same adsorbent were consistent with one another.

388. ———. Chemisorptions of Gases on Iron-Synthetic-Ammonia Catalysts. Jour. Am. Chem. Soc., vol. 62, 1940, pp. 1732-1740; Chem. Abs., vol. 34, 1940, p. 6156.

Chemisorption experiments were performed on the following Fe-synthetic-NH<sub>3</sub> catalysts; unpromoted catalyst containing 0.15% Al<sub>2</sub>O<sub>3</sub>, singly promoted catalyst containing 10.2% Al<sub>2</sub>O<sub>3</sub>, doubly promoted catalyst containing 1.59% K<sub>2</sub>O and 1.3 Al<sub>2</sub>O<sub>3</sub>, catalyst containing 1.07% K<sub>2</sub>O, singly promoted catalyst containing 1.03% Al<sub>2</sub>O<sub>3</sub> and 0.19 ZrO<sub>2</sub>, and doubly promoted catalyst containing 0.35% Al<sub>2</sub>O<sub>3</sub> and 0.08 K<sub>2</sub>O. The weights and reduction schedule (time and temperature) are given for the preparation of these catalysts. The chemisorptions of O<sub>2</sub> and CO at -183° and -78°, CO<sub>2</sub> at -78 and 0°, N<sub>2</sub> at 400°-450°, H<sub>2</sub> at -78° (type A), and H<sub>2</sub> at 100° (type B) were studied on these catalysts. From the investigation of these adsorptions individually and from their mutual inhibitory effects the following conclusions are drawn: The CO<sub>2</sub> chemisorption is located on the surface alkali molecules, and the 5 other chemisorptions on the surface of Fe atoms. CO and CO<sub>2</sub> are chemisorbed as

molecules, N and H as atoms, O probably as ions. Both the Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O promoters are strongly concentrated on the surfaces of singly and doubly promoted catalysts. The alkali promoter is very intimately mixed with Fe atoms on the surface. The Fe surface is heterogeneous; the heterogeneity probably is due to differently developed crystal faces. The molecular CO and CO<sub>2</sub> chemisorptions are purely surface adsorptions; O ions penetrate several layers below the surface; N and H atoms probably do not penetrate below the surface but migrate to Fe atoms located under surface promoter molecules. Both the K<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> promoters give evidences of specific chemical effects.

389. BRUNAUER, S., EMMETT, P. H., AND TELLER, E. Adsorption of Gases in Multimolecular Layers. Jour. Am. Chem. Soc., vol. 60, 1938, pp. 309-319; Chem. Abs., vol. 32, 1938, p. 4037.

Polarization theory of multimolecular adsorption discussed critically. The adsorption energy, owing to attraction of dipoles induced into a nonpolar gas such as A, is insufficient to constitute a major portion of the binding energy between adsorbed layers. Adsorption-isotherm equations for multimolecular adsorption are derived on the assumption that the same forces that produce condensation are responsible also for multimolecular adsorption. Numerous applications of the equations are given to experimental adsorption isotherms.

390. BRUNAUER, S., JEFFERSON, M. E., EMMETT, P. H., AND HENDRICKS, S. B. Equilibria in the Iron-Nitrogen System. Jour. Am. Chem. Soc. vol. 52, 1931, pp. 1778-1786; Chem. Abs., vol. 25, 1931, p. 3550.

At atmospheric pressure the % NH<sub>3</sub> in a gaseous H<sub>2</sub>-NH<sub>3</sub> mixture in equilibrium with an Fe-Fe<sub>3</sub>N mixture is 37±2 at 400° and 14.5±1 at 575°. The % NH<sub>3</sub> in a similar equilibrium with Fe<sub>3</sub>N-Fe<sub>2</sub>N is 77±2 at 400°, 70±2 at 444°, and 57±1.5 at 500°. The composition and lattice dimensions of the phases with an Fe:N ratio of 2:2.7 in equilibrium with various H<sub>2</sub>-NH<sub>3</sub> mixtures is determined at 400° and 444°. The dissociation pressure of Fe<sub>3</sub>N is calculated as 3 x 10<sup>-10</sup> atm. at 450°.

391. BRUNAUER, S. Quality of Synthetic Gasoline From Natural Gas. Ind. Eng. Chem., vol. 41, No. 11, 1949, pp. 2511-2515.

Gasoline produced in this country by the fluidized iron-catalyzed hydrogenation of CO is of much higher quality than that produced commercially in Europe by the Fischer-Tropsch, fixed-bed, Co-catalyzed process. In contrast to the high-boiling, paraffinic material produced over Co, the hydrocarbons produced by the American process are relatively low-boiling and highly olefinic. The olefin characteristic permits the conversion of the gasoline to a high-octane fuel or blending stock by a simple catalytic treatment. A 7-lb. Reid vapor pressure, 400° F. end-point naphtha has a C. F. R. M. clear octane of 82 and a C. F. R. R. octane of 92. The synthetic fuel blends normally in straight-run and cracked products.

BRUNS, B. See abs. 332, 333.

392. BRUNSCHEWIG, R. [Synthetic Liquid Fuels: Problems of the Rational Utilization of Mineral Fuels.] Chaleur et ind., vol. 9, 1928, pp. 143-151; Chem. Abs., vol. 22, 1928, p. 2256.

Address including some information on Fischer's process for hydrogenating at 700° and atmospheric pressure with a catalyst producing aromatics and paraffins.

393. ———. [Economic Aspects of the Synthesis of Liquid Fuels.] Conférences-rapports sur les combustibles, Sec. tchecoslov. soc. chim. ind., vol. 24, 1930, pp. 51-58; Chem. Abs., vol. 24, 1930, p. 4610.

Address.

394. ———. [French Problem of Substitute Fuels.] Rev. ind. minière, No. 421, 1938, pp. 313-328.

General consideration of synthetic fuels and methods of synthesis in other countries with an explanation of the position in France with respect to alcohol fuels, coal-carbonization products, and hydrogenation.

395. BRATZKUS, M. [Processes for the Production of Light Oils for Internal-Combustion Engines.] Chim. et ind., vol. 14, 1925, pp. 171-185, 358-362; Chem. Abs., vol. 20, 1926, p. 102.

Van't Hoff's equation,  $dlmK/AT=Q/TR^2$ , is expressed as follows: Any chemical reaction can be directed and accelerated in a certain direction by continuous and simultaneous external variations in pressure, temperature, and concentration, acting in a direction contrary to that of the corresponding variations caused by the desired reaction. Bratzkus suggests that the desired variations in pressure, temperature, and concentration can easily be obtained by operating in a compressor constructed and operated substantially as a diesel engine. Application of such a method for cracking or hydrogenation under various conditions (exothermic and endothermic reactions), for the treatment of petroleum, tar oils, turpentine, fats, sugars and molasses, cellulose compounds, and coal, and for the synthesis of light oil from CO, CO<sub>2</sub>, and H<sub>2</sub>, is discussed and compared with corresponding processes at present in use or proposed. Very high temperatures and pressure could be used, and catalyzers could be eliminated.

396. BRYANT, W. M. D. Calculations on Water-Gas Equilibrium. Choice of Suitable Molecular-Heat Equations. Heat of Reaction and Free Energy as a Function of the Temperature. Ind. Eng. Chem., vol. 23, 1931, pp. 1019-1024, 1809; Chem. Abs., vol. 25, 1931, p. 5612.

Thermal and equilibrium data for the water-gas reaction are assembled and discussed.  $\Delta H_{298}$  for the reaction  $C(s) + H_2O(g) = CO(g) + H_2(g)$  is calculated to be 9,731 cal. This value is combined with molecular-heat equations from several sources to yield expressions for  $\Delta H$  as a function of the temperature. These equations, in turn, are used to show the order of agreement existing between molecular-heat of different sources. For this reaction, specific-heat equations of Lewis and Randall, of Eucken, and of Eastman give similar results. Partington and Shilling's equations do not agree with these results. Expressions for the free-energy change,  $\Delta F^\circ$ , and its temperature coefficient is derived, as well as for the corresponding reaction isochores. The equilibrium value of Neumann and Köhler at 1,250.1°K. is used to determine the integration constants. The molecular-heat equations of Lewis and Randall, of Eucken, and of Eastman satisfactorily reproduce the experimental equilibrium constants in the water-gas reaction. Partington and Shilling's molecular-heat equations fail to reproduce these values. Numerical results ranging 6,828-6,750 cal. are obtained, depending on the specific heats used. These values constitute the first step in a recalculation of the free energy of formation of CO and CO<sub>2</sub>.

397. BUECHNER, —. Oxidizability of Cobalt Catalyst. FIAT Reel K29, 1938, frames 7,095-7,108; PB 70,218; TOM Reel 296.

Operating instruction for the determination of trivalent Co is worked out as a result of tests on the determination of the content of trivalent Co in Co catalysts. 1 drawing, 2 tables, 8 graphs.

398. ———. [Recovery of Thorium From the Thorium Catalyst Suspensions.] FIAT Reel K-29, 1938, frames 6,985-7,004, 7,032-7,036, 7,091-7,094, 7,120-7,133; PB 70,218; TOM Reel 296.

Describes improved sulfate process for the recovery of Th from the preliminary precipitation suspension. Gives experiences in 2 large regeneration installations.

399. ———. [Catalysts for an Increased Preparation of Paraffin.] FIAT Reel K29, 1938, frame 6,953; PB 70,218; TOM Reel 296.

Supplement to FIAT Reel K29, frames 6,941-6,944, in which Co catalyst containing Mn is described. Separation of the obtained quantity of paraffin into 1 portion (Gatsch) with a solidification point under 50° and into another portion with a solidification point over 50° is given.

400. ———. Examination of the Reaction Water of the Iron-Catalyst Synthesis. FIAT Reel K 29, 1941, frames 7,242-7,249; PB 70,218; TOM Reel 296.

Analysis of products dissolved in the reaction water in the Fe-catalyst synthesis and description of the analytical method. Since the reaction water contains only about 4 gm. EtOH/l, a technical extraction scarcely seems possible. 5 tables.

401. ———. Alcohol-Forming Catalysts. FIAT Reel K 29, 1945, frames 7,214-7,215; PB 70,218; TOM Reel 296.

Constituents and operating data of 3 alcohol-forming Fe catalysts. 1 of them is proposed as a standard catalyst.

402. BUECHNER, —, HECHEL, H., AND ROELEX, O. Behavior of Inorganic Impurities in Kieselguhr. FIAT Reel K-20, frames 99-102, 1939; PB 70,211; TOM Reel 287, frames 99-102.

Seasonal variations in the quality of kieselguhr 12 o. were observed. Investigation led to the opinion that these variations are due to storage in the open. When kieselguhr lies in heaps, the Fe oxidizes and the S is transformed into H<sub>2</sub>SO<sub>4</sub>. These processes are termed "cold combustion" and are said not to occur when kieselguhr is stored flat. When heated to 400°-500°, Fe and S form ferrous sulfate. When the kieselguhr is heated to 1,000° the ferrous sulfate is transformed into ferric silicate. The proportion of Fe, which with the O<sub>2</sub> of the air has already been transformed to the ferrous form, remains unchanged. Ca, S, and Al cause no changes by storage.

BUELOW, H. See abs. 3137.

BUFFLEB, H. See abs. 2679, 2680, 2681, 2682.

BUFORD, C. E. See abs. 1268.

403. BRUCE, G. [Coal Transformation.] Ullmann, Enzyk. Tech. Chem., vol. 6, 2d ed., 1930, pp. 643-670.

Patent and literature listing and summary of the Fischer-Tropsch and the Bergius processes.

404. BRUCE, P. E., AND KERLOGUE, R. H. Determination of the Surface Area of Powders by Means of Low-Temperature Adsorption Isotherms. Jour. Soc. Chem. Ind., vol. 66, 1947, pp. 377-381.

Simple routine procedure for the determination of the surface area of powders by means of low-temperature adsorption isotherms is described with full experimental and mathematical detail. Method of interpretation has been formulated permitting the elimination of the "dead-space" determination for routine procedure where the substance is known to give an S-shaped isotherm. Apparatus and the method are based on previous work of Brunauer and Emmett.

BULANOVA, T. F. See abs. 1705.

405. BULLARD, R. H. Société belge l'azote, Liège; CIOS Report II-11, 1945, 6 pp.; PB 170; TOM Reel 196; Fuel Abs., vol. 3, abs. 454.

During the war this plant produced compressed CH<sub>4</sub> gas from coke-oven gas for use as an auto fuel. MeOH is made now by catalytically cracking coke-oven gas to CO and H<sub>2</sub> and reducing it to MeOH. The catalyst used and the conditions of operation were not discussed but have been patented. The resulting gas consists of 10% N<sub>2</sub>, 30% CO, and 60% H<sub>2</sub>. Production of MeOH is

20,000 liters/day. A new water-gas plant has been installed with a capacity of 80,000 m<sup>3</sup>/day. Nearly all the MeOH produced is converted to CH<sub>2</sub>O. Before the war the company had a pilot plant for the hydrogenation of coal-tar oils producing 85-90 octane gasoline, but in 1940 it was dismantled, although in 1939 it produced 600 tons of gasoline for the Belgian army.

406. BUNTE, K. [Residual Gas From Fischer-Tropsch Synthesis as Town's Gas.] Gas-u. Wasserfach, vol. 83, 1940, pp. 497-499; British Abs., 1948, B I, p. 64.

Composition of the gas varies rather widely, mean values being: CO, 17%; CO<sub>2</sub>, 9%; CH<sub>4</sub>, 33%; H<sub>2</sub>, 20%; N<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>, 0.7 vol. %. The calorific value is within the town's gas range but the high density and low flame speed renders its behavior unsatisfactory unless it is mixed with 2.5 vol. of normal town's gas.

407. BUNTE, K., AND GIESSEN, A. [Influence of Coke Reactivity on Water-Gas Formation.] Gas-u. Wasserfach, vol. 73, 1930, pp. 241-247; Chem. Abs., vol. 24, 1930, p. 2862.

Experimental results indicate that the reactivity of various cokes with respect to water vapor decreases in the following order: Wet-quenched, low-temperature lignite coke; wood charcoal; dry-quenched, low-temperature lignite coke; semicoke; wet-quenched gas coke; dry-quenched gas coke and oven coke. This is in the same order as determined for O<sub>2</sub> alone and O<sub>2</sub> in CO. (Bibliography given). Some relationship can be noted between water-vapor decomposition and ignition temperature of the coke, but this is obscured by the effect of undecomposed steam passing through the fuel bed on the water-gas equilibrium in the gaseous phase. This effect is difficult to evaluate as it is practically impossible to draw gas samples directly from the fuel surface, and, in addition, equilibrium is not reached in the water-gas reaction, even at the higher temperatures.

408. BUNTE, K., BRÜCKNER, H., AND SCHENK, P. [Synthesis of Benzine Hydrocarbons From Methane.] Gas-u. Wasserfach, vol. 84, 1941, pp. 377-381, 391-396; Chem. Abs., vol. 36, 1942, p. 3158.

Only 12 wt. % (maximum yield) of CH<sub>4</sub> could be converted into liquid products by passing it at a rate of 100 l./hr. through a Pythagoras tube heated at 1,200° in an electric furnace. The exit gases had the composition: C<sub>2</sub>H<sub>6</sub>, 1.8%; C<sub>3</sub>H<sub>8</sub>, 2.0%; C<sub>4</sub>H<sub>10</sub>, 3.8%; H<sub>2</sub>, 45.9%; CH<sub>4</sub>, 50.3%. The yield of liquid products was: Light oil 39.5 gm./m<sup>3</sup> and tar 86.0 gm./m<sup>3</sup>. The effect of size of reaction tube (13, 10, 6, and 4 mm. diam.) was studied. Behavior of catalysts of groups I-III supported on porcelain was investigated, with the same apparatus. Most metals and metallic oxides, especially those of the Fe group, promote direct decomposition of CH<sub>4</sub> into C and H<sub>2</sub>; the decomposition rate is accelerated and the reaction temperature lowered by such catalysts. The small increase in the yield of liquid hydrocarbons effected by U, W, and Mo apparently is not due to catalytic action. Ag has a slight catalytic action, 13.1 wt. % of CH<sub>4</sub> being converted into liquid products. At 1,150° and at a rate of 40 l./hr. the exit gases consisted of: C<sub>2</sub>H<sub>6</sub>, 2.7%; C<sub>3</sub>H<sub>8</sub>, 2.3%; C<sub>4</sub>H<sub>10</sub>, 5.0%; H<sub>2</sub>, 47.4%; and CH<sub>4</sub>, 47.6%. The yield of liquid products was: Light oil 38.1 gm./m<sup>3</sup> and tar 33.6 gm./m<sup>3</sup>. Liquid hydrocarbons formed by the thermal decomposition of CH<sub>4</sub> are almost entirely aromatic in character, the main constituents being C<sub>6</sub>H<sub>6</sub>, toluene, C<sub>8</sub>H<sub>8</sub>, and anthracene (typical analyses given). The constitution of the oil depends chiefly on the reaction temperature and reaction time and not to any marked extent on the type of catalyst used.

409. BUNTING, R., AND HUNTER, W. Synthesis-Gas Production in the Fischer-Tropsch Process. Interrogation of Dr. Koebel. Bib. Sci. Ind. Repts., vol. 10, No. 2, 1948, p. 184; PB 92,120.

1. Gas manufacture, Germany. 2. Fischer-Tropsch process. 3. Gas synthesis, Germany. 4. Catalysts Fe, Germany. 5. Fischer-Tropsch Plant, Courrières-Kuhlmann Oil, Harnes, France.

410. BURGART, P., AND GRAETZ, A. [Synthesis of Liquid Fuel.] Tech. moderne, vol. 19, 1927, pp. 705-713, 743-749; Chem. Abs., vol. 22, 1928, p. 676.

Review showing status of investigations in this field.

BURGOYNE, E. E. See abs. 7.

411. BURKE, S. P. Use of Oxygen in the Manufacture of Gas-Gas Production Subcommittee Report. Am. Gas Assoc. Monthly, vol. 26, September 1944, p. 374; U. O. P. Co. Lib. Bull., abs. 39, 1944.

It appears probable that, if the air is replaced by 98% pure O<sub>2</sub> in the manufacture of blue gas, a gas of approximately 300 B. t. u. can be produced continuously without increasing the clinking difficulties. Approximately 220 cu. ft. of O<sub>2</sub> is necessary to produce 1,000 cu. ft. of blue gas. The use of O<sub>2</sub> means a large increase in the gas-making capacity of the gas producer. A conservative estimate for the cost of 95% O<sub>2</sub> places it at \$0.14 per M cu. ft. Electrolytic production of H<sub>2</sub> and O<sub>2</sub> under pressures up to 300 atm. has been reported as successful from sources in Germany and Sweden. At such a pressure there is a depolarizing effect and a reduction of solution resistance such that the electrical efficiency is improved enough to offset the energy of compression; the electrical requirement is no greater than that necessary at atmospheric pressure. The size and cost of such electrolytic plants are far less than for a plant for making O<sub>2</sub> from the air.

BURNS, J. See abs. 2534.

BURNS, R. M. See abs. 3335.

412. BURRELL, G. A. Hydrogenation of Coal Processes. Oil Gas Jour., vol. 27, October 18, 1928, p. 56.

Motor fuels may be prepared from coal by hydrogenation of coal (Bergius process) or of CO. Water gas (CO and H<sub>2</sub>) is made to combine in the presence of various catalysts with or without pressure. Processes in active stages of development in Germany are the Bergius process (pressure hydrogenation of coal), the I. G. Farbenindustrie process (pressure hydrogenation of coal with a catalyst), and the Fischer-Tropsch process (CO+H<sub>2</sub>+a catalyst with or without pressure); in France the Patart process (CO+H<sub>2</sub>+a catalyst+high pressure) and the Audibert process (CO+H<sub>2</sub>+a catalyst+pressure); and in England the Nash process (CO+H<sub>2</sub>+a catalyst).

413. BURSTIN, H. [Synthesis of Fuels for Airplane Motors.] Przegląd Chem., vol. 2, 1938, pp. 250-264; Chem. Zentralb., 1939, II, p. 1423; Chem. Abs., vol. 35, 1941, p. 4178.

Topics considered include properties of fuels, composition and properties of the more important hydrocarbons, gases, and cracked benzenes, processes of selective extraction and polymerization of the products of cracking, benzene substitutes and partial substitutes (ethers, alcohols), antiknock agents (alcohol, benzene, PbEt<sub>2</sub>), liquefaction of coal and syntheses for benzene and Diesel fuels, production and synthesis of airplane lubricants, and the lubricating efficiency and resistance to oxidation of these oils.

414. BURWELL, R. L., JR., AND TAYLOR, H. S. Activated Adsorption of Hydrogen and Carbon Monoxide on Zinc Oxide—Effect of Water Vapor. Jour. Am. Chem. Soc., vol. 58, 1936, pp. 1753-1755; Chem. Abs., vol. 30, 1936, p. 7954.

H<sub>2</sub>O vapor minimizes surface reduction of ZnO catalysts at lower temperatures. It is strongly adsorbed from gas mixtures by those fractions of the ZnO sur-

face to which the gas mixture has access. Saturation of ZnO surfaces by H<sub>2</sub>O markedly inhibits the activated adsorption of H<sub>2</sub> and CO.

415. ———. Adsorption and Decomposition of Carbon Monoxide on Zinc Oxide Catalysts. Jour. Am. Chem. Soc., vol. 59, 1937, pp. 697-699; Chem. Abs., vol. 31, 1937, p. 4882.

Study of the activated adsorption of CO on ZnO at temperatures of 184° and higher shows that concurrently with the activated adsorption some decomposition into CO<sub>2</sub> and C occurs. C deposited on the catalyst is removed by H<sub>2</sub> at 184° and above, presumably as CH<sub>4</sub>.

Brschow, H. F. See abs. 1625.

Brsr. M. See abs. 2106.

416. BUSINESS WEEK. Petroleum Substitutes. July 21, 1945, p. 74; Nat. Petrol. News, vol. 37, No. 36, R744, Sept. 5, 1945.

Hydrocarbon Research, Inc. announces that it will construct a commercial Synthine (Fischer-Tropsch) plant in East Texas. The plant will have a capacity of 7,000 bbl./day of finished products, 80-85% of which will be high-octane motor gasoline. Production will be at the rate of 1 bbl. of oil/10,000 cu. ft. of gas. The process, developed in the past 20 months, has been sponsored by 3 oil producers: The Magnolia Petroleum Co., the LaGloria Corp., and the J. S. Abercrombie Co. The process is based on German laboratory research applied to American oil-industry techniques concerning plant design and construction and the use of cheaper catalysts. The plant, it is said, will be constructed at a fraction of the cost of similar German plants and will produce a higher quality gasoline.

417. ———. Fuel Research in Canada. No. 890, 1946, p. 112.

It is reported that the Canadian Government is abandoning its active participation in synthetic-liquid-fuels research and, instead, plans to appoint a fuel-research board representing both the Government and of private industry and assign to it the responsibility of

following current research in the United States and of drawing up a new liquid-fuel program for the Dominion. Plans approved by Parliament for a \$750,000 coal-hydrogenation pilot plant will be postponed, since the Canadian Government sees no economic future for a synthetic-fuels industry in eastern Canada based on high-cost Nova Scotia coal. The same applies to the Pacific coast region. Attention will, however, continue to be given to the Mid-Continent region and research on natural gas, coal, and natural bitumen from Alberta tar sands will be continued.

418. BÜTEFISCH, —. Synthetic-Oil Production in Germany. BIOS Final Rept. 1697 (Interrogation Rept. 667), 1946, 26 pp.; PB 92,191.

A questionnaire directed to Dr. Bütefisch with his replies, which bring out several points of comparison between the Fischer-Tropsch and coal-hydrogenation processes. Data on plants, plant capacity, products, production costs, and uses of and properties of the products are reviewed. It is concluded that the Fischer-Tropsch process should be regarded as a purely chemical process yielding hydrocarbons, where as the hydrogenation process was mainly suitable for making fuel oils but not chemicals.

419. BUYLLA, B. A., AND PERTIERRA, J. M. [Synthesis of High Hydrocarbons From Water Gas.] Anales soc. espan. fis. quim., vol. 27, 1929, pp. 23-38; Chem. Zentralb., 1929, I, p. 2846; Chem. Abs., vol. 23, 1929, p. 2810.

In the catalytic reduction of CO contained in water gas by CuO, Co<sub>2</sub>O<sub>3</sub>, and MnO<sub>2</sub>, a test was made at 254°, which was lower than any previous temperature used. Here the contraction was less than at higher temperature, but the yield of liquid and solid hydrocarbons was higher. The necessity of extreme purification of water gas to maintain activity of a catalyst activated by successive oxidations and reductions is shown.

BYRNE, B. J. See abs. 2448.

BYSTRÖM, H. See abs. 1388.

suggests a way in which the rings may have been formed.

420b. CAIN, D. G., WEITKAMP, A. W., AND BOWMAN, N. J. Products of the Hydrogenation of Carbon Monoxide Over an Iron Catalyst. Oil-Soluble Oxygenated Compounds. Am. Chem. Soc., 121st Meeting Abs., March-April, 1952, p. 11-M.

The oxygenated compounds in the oil stream produced by hydrogenation of CO over an Fe catalyst are higher homologs of those in the H<sub>2</sub>O stream. The main components are acids, alcohols, and carbonyl compounds of the aliphatic series. Yields of these classes decrease with increasing C number >5. At a given C number, the ratio of the molar quantities of each of the main components to the total molar quantity of oxygenated compounds and hydrocarbons is approximately constant. The alcohols appear to be more closely related structurally to the aliphatic hydrocarbons than are the acids. Branched isomers are more prevalent in the acids. Olefinic unsaturation and aromatic rings are present in some oxygenated molecules, but molecules containing 2 oxygenated groups have not been detected.

421. CALCOTT, W. S. Activities of I. G. Farbenindustrie A.-G., Leuna. Soap Substitute. CIOS Rept. XXII-19; TOM Reel 196; PB Rept. 187, 1945, 8 pp.

One of the important products made at Leuna was a soap substitute called Mersol, made from the Kogasin fraction of Fischer-Tropsch oil. As received, the Kogasin contained both oxygen derivatives and un-

420. CADMAN, W. H. Fuels Produced by Hydrogenation and Synthetic Processes. Ann. Rev. Petrol. Technol., vol. 6, 1941, pp. 155-165.

Review of the commercial developments in Great Britain and abroad in 1940.

CADY, W. E. See abs. 3642b.

420a. CADY, W. E., LAUNER, P. J., AND WEITKAMP, A. W. Products of the Hydrogenation of Carbon Monoxide Over an Iron Catalyst. Aromatic Hydrocarbons. Am. Chem. Soc., 121st Meeting Abs., March-April, 1952, p. 10-M.

Aromatics constitute about 6 wt. % of the hydrocarbons obtained in the hydrocarbon-synthesis process. They were separated by adsorption on silica gel and by distillation and were analyzed by ultraviolet and infrared spectroscopy. Benzene is present in traces, but successive C-number fractions contain increasing concentrations of aromatics. Monocyclic, bicyclic, and tricyclic aromatics occur in proportions that decrease with the number of aromatic rings. Some of the aromatic hydrocarbons contain a nonaromatic ring fused with the nucleus. Olefinic unsaturation is an important feature of the high-molecular-weight aromatics. Some unsaturation may be in the rings of compounds of the indene or the dihydronaphthalene series; the remainder is side-chain unsaturation. Aromatic rings occur to a small extent in the structures of the oxygenated compounds. In the benzene series, monoalkyl and o-dialkyl isomers predominate. A regular pattern of alkylbenzene isomer distribution

saturated compounds, which were eliminated by catalytic hydrogenation over a Ni tungstate catalyst at 200 atm. and 300°-350°. A mixture of straight-chain hydrocarbons was obtained containing the compounds from  $C_8H_{18}$  to  $C_{12}H_{26}$ , but chiefly  $C_{10}H_{22}$ . This mixture was treated with  $SO_2$  and Cl while being irradiated with ultraviolet light at 30°-40°. The reaction is carried to only 70% completion to avoid formation of excessive amounts of disulfonyl chloride, which is useless for soap production. The sulfonyl chloride is used for soap making, being saponified with other soapmaking materials. A cresol ester is prepared from sulfonyl chloride and used as a plasticizer for polyvinyl chloride. The Na salt, called Mersolat, is made by saponifying the Mersol at 70° with a 10% NaOH solution. The oil is separated from the sodium alkyl sulfonate by decantation, chlorinated, and used as a solvent. At the peak of operation about 4,500 tons per month of Mersol were being produced. Equipment and process are described.

422. CALDWELL, J. M. AND SMITH, G. H. Mersol and Hostapon Processes. I. G. Farbenindustrie A.-G., Höchst. BIOS Final Rept. 1222, 1946, 9 pp.; PB 79,310.

Further information than is given in BIOS Final Rept. 478 on the manufacture of Mersol-type detergent products from a hydrogenated Fischer-Tropsch cut of boiling range 220°-320°, Mepasin. Mersol H<sub>2</sub> is produced by the action of  $SO_2$  and Cl on Mepasin. Mersol H<sub>2</sub> can be converted to Mersolat by reacting with caustic soda in 10% solution. Hostapon is produced by the direct action of  $SO_2$  and O<sub>2</sub> on Mepasin, using light or acetic anhydride as catalyst. The detergent properties of Hostapon are essentially the same as Mersolat. Gives details of methods.

423. CALVERT, G. C. Synthetic Alcohols and Liquid Fuels. Chem. Age, vol. 5, 1921, p. 153; Chem. Abs., vol. 15, 1921, p. 3735.

Calvert has developed a method of converting C into water gas and mixing this with other gases, according to the product desired. Utilization of wood waste, charcoal, or carbonizable tropical matter should yield fuel MeOH at \$19/ton. Details of the process are withheld. The ratio of efficiency of MeOH to gasoline for use in internal-combustion engines is 5:4.

424. CAMPBELL, E. D., FINK, W. L., AND ROSS, J. F. Iron-Iron Carbide Equilibrium in Dry Hydrogen at 950°. Jour. Iron Steel Inst. (London), No. 108, II, 1923, pp. 173-178; Chem. Abs., vol. 18, 1924, p. 612.

Results of several experiments to determine the amount of C transferred from a solution of carbides in Fe to one of lower concentration. The loss in weight of the samples indicates formation of a solution of Fe carbides, which then react with H<sub>2</sub> to form gaseous hydrocarbons. It is suggested, from the small amount of greasy substance found in the reaction tubes, that the gaseous C compounds are not entirely CH<sub>4</sub> but that a part at least were hydrocarbons of higher molecular weight.

424a. CAMPBELL, W. M. AND JOHNSTONE, H. F. Reactions of Hydrogen and Carbon Monoxide in a Tubular Reactor With Iron-Copper Catalyst. Ind. Eng. Chem., vol. 44, 1952, pp. 1,570-1,575; Chem. Abs., vol. 46, 1952, p. 8,349.

Some of the factors affecting the Fischer-Tropsch synthesis were studied in order to learn more about the reaction mechanism. The reactor consisted of a porous aluminum tube, impregnated with the catalyst, through which the gases flowed longitudinally. Stable and reproducible Fe-Cu catalysts which produce CO and hydrocarbons from synthesis gas at atmospheric pressure were developed. When treated with steam

and CO at 250° the activity of these catalysts increases. At 280° the activity drops rapidly and eventually reaches a period of constant activity where the only products are CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and CO. The loss in activity due to H<sub>2</sub>S poisoning is a linear function of the amount of S absorbed, and when about 0.5 atom of S/atom of metal is taken up the activity is 0. Catalysts producing CO are active for the water gas shift reaction. Heating at 310° in the presence of H<sub>2</sub> and CO destroys the synthesis reaction activity, but does not change the shift reaction activity. H<sub>2</sub>S destroys the activity for both reactions. The shift reaction activity of a H<sub>2</sub>O producing catalyst can be increased by increasing the H<sub>2</sub> concentration in the feed gas. These results are definite proof of the existence of 2 types of active centers, 1 for the shift reaction and the other for the synthesis reaction. A dual reaction mechanism is proposed, by which paraffins are formed by Craxford's mechanism, and olefins are formed by simply splitting the (CH<sub>2</sub>)<sub>n</sub> chain off the surface. In a CO-producing catalyst, the metal active centers must be present in clusters principally.

425. CANDEA, C. AND KÜHN, J. [Decomposition of Methane and Petroleum Hydrocarbons With Steam.] Bull. sci. école polytech. Timisoara, vol. 5, 1934, pp. 225-232; Chem. Abs., vol. 29, 1935, p. 8302.

Reaction of steam upon CH<sub>4</sub> and various petroleum fractions, including a distillation residue, was studied in quartz and steel tubes with various catalysts and a wide range of temperatures. Natural gas containing 96.4% CH<sub>4</sub> was almost completely transformed into H<sub>2</sub> (70%) and CO (20%) at 1,000° with an Fe-Ni-Mn catalyst, a ratio of steam to natural gas of 1:3, and time of contact 20 sec. Kerosine produced 30% H<sub>2</sub> and 70% CO under similar conditions, except that the time of contact was less. A very good illuminating gas was obtained from the petroleum residue at 800°-900°. This gas would also be suitable as fuel for gas engines.

426. CANTELO, R. C. Thermal Decomposition of Methane. I. Jour. Phys. Chem., vol. 28, 1924, pp. 1036-1048; Chem. Abs., vol. 19, 1925, p. 204.

Calculation of the equilibrium constant for the decomposition of CH<sub>4</sub> into C and H<sub>2</sub> shows this reaction to be almost complete at 700°. Various contact catalysts were, therefore, tried to hasten the formation of C black at this temperature. Asbestos impregnated with Ni-Ni oxide was most effective.

427. ———. Thermal Decomposition of Methane. II. Jour. Phys. Chem., vol. 30, 1926, pp. 899-901; Chem. Abs., vol. 20, 1926, p. 2934.

Equations for velocity of decomposition of CH<sub>4</sub> to C and 2 H<sub>2</sub> were derived and applied to experimental results at 985°. The reaction was only 36% complete after 1 hr. The velocity was abnormally high for 5 min. until the walls were covered with C. The velocity constant is of the order of 0.15.

428. ———. Methane Equilibrium. I. Jour. Phys. Chem., vol. 30, 1926, pp. 1641-1645; Chem. Abs., vol. 21, 1927, p. 522.

Equilibrium constants for the reaction  $C+2H_2 \rightleftharpoons CH_4+21,730 \text{ cal.}$ , were calculated by Saunders' equation  $\log K_p = (4583/T) - 1.75 \log T + 0.000630 T - 0.7$  over the temperature range 500°-1,100°. With these values of  $K_p$  the equilibrium concentrations of CH<sub>4</sub> and H<sub>2</sub> are calculated to be: Temperature 500°, % CH<sub>4</sub>, 63.9; % H<sub>2</sub>, 36.1; 600°, 37.9; 62.1; 700°, 16.3; 83.7; 750°, 13.0; 87.0; 800°, 7.5; 92.5; 850°, 4.5; 95.5; 900°, 3.6; 96.4; 1,000°, 2.0; 98.0; 1,100°, 0.8; 99.2. These values reconcile the results of earlier investigators. The equilibrium concentrations of CH<sub>4</sub> and H<sub>2</sub> obtained from the catalytic decomposition of pure CH<sub>4</sub> were measured at 565°, 670°, and 770°. The cata-

lyst was prepared by ignition of pure NiNO<sub>3</sub> deposited on asbestos fibers. This material was then reduced in H<sub>2</sub>. The gas mixture was circulated over the heated catalyst until no further increase in volume was observed. The equilibrium composition of the gas was found by analysis to be: Temperature 565°, % CH<sub>4</sub>, 32.7; % H<sub>2</sub>, 58.9; % N<sub>2</sub>, 6.5; % CO, 1.4; 670°, 24.4, 68.8, 5.3, 1.9; 770°, 9.2, 85.9, 3.7, 1.2. The values of  $K_p$  corresponding to these results are: 565°, 0.95; 670°, 0.47; 770°, 0.12.

429. ———. Methane Equilibrium. II. Jour. Phys. Chem., vol. 31, 1927, pp. 124-130; Chem. Abs., vol. 21, 1927, p. 849.

Equilibrium constants for the reactions that might conceivably occur along with the thermal decomposition of C<sub>2</sub>H<sub>6</sub> are calculated by means of the Nernst approximation formula. The calculations are tabulated for 200°, 400°, 600°, and 800°. The reactions with their increase in heat content are:

$C_2H_6 = 2C + 2H_2 - 14,600 \text{ cal.}$ ;  $C_2H_6 = C_2H_4 + H_2 + 43,500 \text{ cal.}$ ;  $3C_2H_6 = C_2H_6 + 3H_2 - 32,500 \text{ cal.}$ ;  $C_2H_6 = 2C + 3H_2 + 23,300 \text{ cal.}$ ;  $C_2H_6 = C_2H_4 + H_2 + 37,900 \text{ cal.}$ ;  $C_2H_6 = C_2H_2 + 2H_2 + 81,400 \text{ cal.}$ ;  $3C_2H_6 = C_2H_6 - 163,000 \text{ cal.}$ ;  $CH_4 = C + 2H_2 + 18,900 \text{ cal.}$ ;  $2CH_4 = C_2H_4 + 2H_2 + 52,400 \text{ cal.}$ ;  $2CH_4 = C_2H_2 + 3H_2 + 95,900 \text{ cal.}$  From a consideration of the equilibrium constants it appears that whether the initial system be CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, or C<sub>2</sub>H<sub>4</sub>, the final equilibrium system will be CH<sub>4</sub>, C, and H<sub>2</sub> in the proportions to satisfy this equilibrium. A brief review of the experimental work upon C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> decomposition shows that the above conclusion is supported by the experimental evidence.

430. ———. Methane Equilibrium. III. Jour. Phys. Chem., vol. 31, 1927, pp. 246-250; Chem. Abs., vol. 21, 1927, p. 1538.

In the catalytic decomposition of C<sub>2</sub>H<sub>6</sub> the catalyst most effective is a specially prepared Ni-Ni oxide; at 300° and higher, CH<sub>4</sub> is present in the products, the % of CH<sub>4</sub> increasing with the temperature. C<sub>2</sub>H<sub>6</sub> is stable up to 360° in the presence of a Ni catalyst. Equilibrium constants for the CH<sub>4</sub> equilibrium at 500°-770° were obtained by repeatedly circulating the products of the catalytic decomposition of C<sub>2</sub>H<sub>6</sub> over the Ni catalyst, which are in general agreement with those obtained by other investigators.

431. ———. Methane Equilibrium. IV. Jour. Phys. Chem., vol. 31, 1927, pp. 417-418; Chem. Abs., vol. 21, 1927, p. 2213.

Free energy of formation of CH<sub>4</sub> from H<sub>2</sub> and amorphous C is calculated as  $\Delta F = -19,280 + 10.67 \text{ TlnT} - 0.007867T^2 - 0.067T^3 - 42.2T$ , from which  $\Delta F = -14,500$ .

432. CAPELL, R. G., AMERO, R. C., AND WOOD, W. H. Fuller's Earth as a Binder for Catalysts and Adsorbents. Petrol. Refiner, vol. 25, No. 2, 1946, pp. 69-71.

Florigel is a grade of Florida-Georgia fuller's earth that develops its maximum adsorptive or decolorizing capacity when heated to 1,200° F. and its maximum dehydrating capacity at 600° F. Plastic properties are destroyed at 700° F., and a hard granule is formed resistant to the action of H<sub>2</sub>O or steam. Above 1,200° F. its adsorptive and catalytic properties decline. In investigating the use of Florigel as a binding agent in catalyst manufacture, experimental samples were prepared by mixing a finely ground catalytic base material and a binding agent, kneading in the desired amount of H<sub>2</sub>O and extruding the mixture, drying at 1,200° F., cooling, and testing for crushing strength. A pellet strength of 20 lb., the minimum usually considered acceptable, was obtained with about 8.5% of Florigel, whereas approximately 19% of ball clay was needed for good extrusion. Fine grinding and thorough mixing are essential in increasing pellet strength and use of enough H<sub>2</sub>O to give it the consistency of a

stiff mud. Florigel requires 150% more H<sub>2</sub>O than does ball clay to obtain the same consistency. Additives, such as tannic acid, Na<sub>2</sub>CO<sub>3</sub>, and NaOH, dissolved in the H<sub>2</sub>O improve extrusion characteristics. Florigel was tested as a bonding agent for a synthetic Mg silicate, an excellent decolorizing agent; at about 35% of Florigel, a maximum decoloring capacity was attained and a hardness for commercial use. The following characteristics make Florigel suitable as a binder: Mixed with H<sub>2</sub>O and catalytic or adsorptive materials it is readily pelleted, pressed or extruded; it increases mechanical strength of soft nonplastic materials; it is irreversible with respect to H<sub>2</sub>O; it is porous and insoluble, hence does not detract from the surface area of the material being bound; it is an adsorbent and a catalyst in its own right; it is stable at high temperature.

CAPP, J. P. See abs. 740.

CARLILE, J. H. G. See abs. 450.

433. CARLIN, G. T. German Meat-Packing and Fat and Oil Operations During the War Period. Food Technol., vol. 1, 1947, pp. 404-414; Chem. Abs., vol. 41, 1947, p. 7556.

Synthetic butter was made by means of the Fischer-Tropsch synthesis for the production of fat. Both Co and Fe catalysts were used. The yields of various fatty acid fractions are listed, and the conversion of the fatty acids in triglycerides by esterification of glycerol is discussed. The synthetic butter exhibited the following values: A.I.P. 35°; I number 10; saponification 235; nonsaponifiable matter 0.2%; hydroxyl value 8-10; and free fatty acids 0.5%. Feeding tests indicated that fatty acid chains of odd number were just as valuable in human nutrition as the natural, even-numbered fatty acids. It was claimed that odd-numbered synthetic fats were of value in the feeding of diabetics because acetone bodies are not formed from the odd-numbered C chains. Soaps and lubricating greases were made from fatty acid fractions unsuitable for the manufacture of synthetic butter.

434. CARLSMITH, L. E. Large-Scale Production of Oxygen. FIAT Final Rept. 1120, 1947, 45 pp.; PB 88,840.

This report is a compilation of miscellaneous information on oxygen production not previously recorded. The activities of the Messer Company are discussed and the larger plants built by them are listed. The Kapitza process (Russian) is reported. This is also a process in which low-pressure air is employed. The outstanding feature appears to be the use of a very efficient, compact, radial-flow, expansion turbine. Efficiencies of 81-83% are claimed for it. An energy consumption of 0.28 kw-hr./m<sup>3</sup> of O<sub>2</sub> has been reported compared with 0.445 claimed by Linde and 0.35 suggested for projected large-scale units in the United States.

See abs. 1625.

CARLSON, C. S. See abs. 2325a.

435. CARNEGIE INSTITUTE OF TECHNOLOGY, COAL RESEARCH LABORATORY STAFF. Coal—An Abundant Raw Material for New Chemicals. Chem. Ind., vol. 52, 1943, pp. 202-204.

Mention is made in the discussion of chemicals derived from coal of the possibilities of the Fischer-Tropsch process.

436. CARON, M. H. [Industrial Uses of Oxygen.] Ingenieur, vol. 44, 1947, pp. M51-56; Jour. Inst. Petrol., vol. 34, 1948, p. 28A.

Review of various manufacturing processes of O<sub>2</sub>, together with costs. Various processes in which O<sub>2</sub> can be used are described, including the use of O<sub>2</sub> in the Fischer-Tropsch, Lurgi, and Bergius processes and in underground gasification of coal.

437. CARPENTER, H. C. H., AND SMITH, C. C. Some Experiments on the Reaction Between Pure Carbon Monoxide and Pure Electrolytic Iron Below the A Inversion. *Jour. Iron Steel Inst.*, vol. 98, 1918, pp. 139-197; *Chem. Abs.*, vol. 12, 1918, p. 2523.

Experiments with electrolytic Fe were all conducted in a quartz tube. The reaction temperature was 650° in all except the 1st few experiments. The tube was heated by enclosing it in another quartz tube, which was wound with Ni-Cr wire and suitably packed in a heat-insulating medium. The total impurities in the Fe amounted to only 0.033%. The CO was prepared by dropping pure HCOOH on concentrated H<sub>2</sub>SO<sub>4</sub>. Special precautions were taken with regard to all the other reagents used. The data obtained from the experiments indicate that the reaction between CO and Fe at 650° is of a complex nature and it was not possible to reach a conclusion as to the precise change or changes. It was demonstrated, however, that a substance is formed that appears to be Fe<sub>3</sub>C. The presence of enough CO<sub>2</sub> in the gas prevents the formation of this substance. The addition of H<sub>2</sub> to CO favors the production of the carbide. In most cases, carbonaceous products are formed containing Fe, C, and O.

438. CARR, T. P. *Coke Oven Managers' Association*, Midland Section. Inaugural Address. *Gas World*, vol. 109, No. 2835, Coking Section 12-14, 1938; *Chem. Abs.*, vol. 33, 1939, p. 1124.

Review of developments in the coking industry during the past few years. Process depends for its action on conversion of coke into water gas. The water gas is divided into 2 portions: 1 portion is specially treated in a gas-cracking apparatus, and the cracked gas is then reblended with the remaining portion of the water gas. The net result of this mixture is to give a gas consisting of approximately 30 parts by volume of CO and 60 parts by volume of H<sub>2</sub>. The synthesis gas so produced is then passed over a catalyst consisting of a Co-Th preparation deposited on kieselguhr at atmospheric pressure and at a temperature of approximately 220° C. a mixture of oils is produced, which can be fractionated into gasol, petrol, diesel oil, and paraffin wax. The gasol consists mainly of propane and butane, which can be sold for country-house lighting and heating and is very similar to the Calor gas marketed in England. The diesel oil is of particularly high quality, having a cetane value of 100, while the petrol is of rather low octane value as compared with the spirit obtained from the hydrogenation process. This petrol can, however, be improved by cracking, and further improvements can be obtained by cracking the diesel oil and paraffin wax produced and blending these cracked products with the petrol. At present the motor-fuel production from this process in Germany is at the rate of approximately 600,000 tons per yr., while there is 1 unit in operation in France producing motor fuel at the rate of 13,000 tons per yr. It is impossible to give a detailed list of the various plants operating on the continent, but the above figures of output can be taken as being substantially correct. The actual proportion of coal or coke used for producing 1 ton of motor spirit naturally varies according to the process adopted, since the Fischer-Tropsch process can operate in a number of different ways. For example, coking coal may be converted into coke, which, in turn, is converted into water gas, as already indicated. Lignites or brown coals may be gasified in special producers to give synthesis gas direct without any intermediate coking, materials of the nature of cannel or oil shale may be carbonized, the gas being used for the conversion into synthesis gas and the coke being used for providing the necessary heat for the generation of steam and power for the process, and the large yield of tar from such carbonization being cracked to give high-octane-value spirit. With the conversion of coal into coke, the

amount of coal required to produce 1 ton of primary products may be approximately 5 tons, whereas, with the use of cannels or similar materials, the quantity of coal used may only amount to 2½ tons per ton of spirit produced.

439. CARTER, D. V. *Gas Conservation in West Texas*. *Oil Gas Jour.*, vol. 45, No. 36, 1947, pp. 74, 76, 77, 86.

Paper presented before the American Institute of Mining Engineers in Texas. It is shown how natural-gas resources can be conserved by way of natural gas-line, gas processing, and pressure maintenance. Tabulated statistics are shown covering the production and disposition of gas in West Texas for 1944-45. Another bright feature of utilization is the large-scale production of O<sub>2</sub>, reducing the present cost of \$70 per ton to about \$3 per ton, and its combination with the Fischer-Tropsch or the Hydrocol processes in manufacturing gasoline from natural gas. Current estimates are that it can be produced for \$0.05 per gal. compared with the present cost in the Texas Gulf coast of \$0.07¼. Greatly improved yields from these processes, it is estimated, could extract 17 billion bbl. of gasoline from the 175 trillion cu. ft. of present gas reserve in the United States as compared to 10 billion bbl. of gasoline from our presently known oil reserves of 20 billion bbl. Increased utilization of West Texas gas should result in a higher price for the gas in competition with the manufacture of carbon black.

CARTER, S. R. *See abs.* 338, 339.

440. CASATS, P. L. [The Fischer-Tropsch Synthesis—a Bibliographic Study.] *Combustibles (Zaragoza)*, vol. 6, 1946, pp. 62-75, 120-134.

Cites 184 refs.

CASAZZA, E. *See abs.* 2386.

441. CASSAN, H. [Gas-Forming Reaction in a Gas Generator Not Under Equilibrium Conditions.] *Chaleur et ind.*, vol. 19, 1938, pp. 441-444; *Chem. Abs.*, vol. 32, 1938, p. 7246.

In actual operation of a water-gas generator, equilibrium is not attained, but is approached to an extent depending on the reactivity of the coke, the contact time, etc. The thermal yield, *P*, is defined as the ratio of the heat of combustion of the gas produced to that of the gas resulting from complete reduction of CO<sub>2</sub> and H<sub>2</sub>O to CO and H<sub>2</sub>. *P* is empirically determined to be a function of the volume content and degree of reduction of the CO<sub>2</sub> and H<sub>2</sub>O separately, in the inlet gas. Values of this function are tabulated and plotted.

442. ———. [Water-Gas Reaction.] *Compt. rend.*, vol. 206, 1938, pp. 1296-1299; *Chem. Abs.*, vol. 32, 1938, p. 5187.

Actual yield (*P*) of a water-gas installation is defined as the ratio *R/R<sub>0</sub>*, where *R* is the ratio of the amount of heat obtainable from the gas produced to that produced by burning the C used, *R<sub>0</sub>* is the theoretical maximum ratio, and *P* is calculated on various semiempirical assumptions for varying relative amounts of CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>.

443. CAWLEY, C. M. *Oil From Coal*. *Min. Jour.* (London), vol. 204, 1939, pp. 179-180; *Chem. Zentralb.*, 1939, I, p. 4415.

Review of carbonization, hydrogenation, and synthesis, their practical significance, and a summary of the results of economic and technical investigation of hydrogenation and hydrocarbon synthesis.

444. ———. *Wax Industry in Germany*. *BIOS Final Rept.*, 1831, 1946, 315 pp.

A survey of the production, refining, and utilization of hydrocarbon, natural, montan, and synthetic waxes was made by contacting 65 production and utilization sources, each of which is discussed. The crude-wax

products form a substantial part of the products of the Fischer-Tropsch process employed in nine plants having a combined output of about 500,000 tons per yr. The crude wax products were of 2 kinds: A soft wax (gatsch) boiling mainly below 450° and a hard wax boiling mainly above 450°. The medium-pressure process gave a higher yield of both soft and hard waxes than the normal-pressure process. In the peak year 1943 the total production of soft wax was 46,170 tons and of hard wax 25,830 tons. The properties, treatment, and utilization of these waxes are dealt with fully. Two of the most important uses of hydrocarbon waxes were as the raw materials for the synthesis of lubricating oil and fatty acids. Because Fischer-Tropsch waxes are richer in n-paraffins than petroleum waxes, they are more suitable for these syntheses. Information is given about various methods for determining the amount of oil in wax products. All methods were based on the crystallization of wax from chilled solvents and the washing and purification of the wax. Considerable work had been carried out in the use of chlorinated solvents for the selective separation of waxes. A summary of information on Fischer-Tropsch waxes is made in an appendix by C. C. Hall, pp. 284-303.

445. ———. *Coal, Shale, Peat, and Their Products in 1947*. I. *Fuels Produced by Hydrogenation and Synthetic Processes*. *Rev. Petrol. Technol.*, vol. 9, 1947, pp. 243-262.

Review of developments, with 126 refs.

*See abs.* 1770.

446. CAWLEY, C. M., AND HALL, C. C. *Fuels Produced by Hydrogenation and Synthetic Processes*. *Ann. Rev. Petrol. Technol.*, vol. 5, 1940, pp. 361-388. *Chem. Abs.*, vol. 34, 1940, p. 8228.

Review covering 1939. Krupp-Treibstoffwerk, G. m. b. H., at Essen obtains its raw material from coal by low temperature. Carbonization by the Krupp-Lurgi process. Production of primary product was begun at the end of 1938. A plant at Deschowitz has been recently completed for the Gräflich schaffgottische Benzin G. m. b. H. of the Silesian coal industry.

447. ———. *Synthetic Fuels: The Fischer-Tropsch Process*. *Rev. Petrol. Technol.*, 1941-45, vol. 7, 1947, pp. 292-306.

General review covering commercial development of the Fischer-Tropsch process, processes and plant, catalysts, reaction mechanism, properties, and uses of products.

448. CAWLEY, C. M., AND WOODWARD, L. A. *Hydrogenation and Synthetic Fuels*. *Ann. Rev. Petrol. Technol.*, vol. 3, 1938, pp. 393-409.

Annual review for 1937 of hydrogenation and Fischer-Tropsch processes. 136 literature and patent refs.

449. ———. *Fuels Produced by Hydrogenation and Synthetic Processes*. *Ann. Rev. Petrol. Technol.*, vol. 4, 1939, pp. 393-409; *Chem. Abs.*, vol. 34, 1940, p. 2161. Review of developments in 1938.

450. CAWLEY, C. M., CARLILE, J. H. G., NEWALL, H. E., AND KINGMAN, F. E. T. Experiments on the Production of Toluene From Coal-Tar Products and Other Sources. *Jour. Inst. Petrol.*, vol. 32, 1946, pp. 660-683; *Chem. Abs.*, vol. 41, 1947, p. 3601.

To supply the toluene requirements of Great Britain during the war, 5 sources of processes were investigated on a laboratory scale. One process was the cyclization of n-heptane obtained from Fischer-Tropsch oil. With the aid of CrO<sub>3</sub> catalyst supported on active Al<sub>2</sub>O<sub>3</sub>, about 57% of toluene was obtained at first, later diminishing to 61%.

CHAFFEE, C. C. *See abs.* 873, 874, 875, 876, 877, 878, 8549.

451. CHAFFEE, C. C., THOMPSON, O. F., KING, J. G., ATWELL, H. V., AND JONES, I. H. *Metallgesellschaft-Lurgi, Frankfurt am Main, Germany*. *CIOS Rept.* XXXI-23, 1945, 54 pp. *TOM Reel* 196; *PB Rept.* 12,624.

The following subjects of interest are discussed: III. Japanese-German relationships with brief data on 9 plants; V. Fischer-Tropsch developments, 7 figures; VI. Carbonization. A. Spuelgas or direct heating process, and B. low-temperature carbonization by indirect heating; VII. High-pressure gasification with synthesis gas and O<sub>2</sub> production, 1 figure; VIII. Synthetic lubricating oil Rheinpreussen plant Homberg, 1 fig.

452. ———. *Metallgesellschaft-Lurgi, Frankfurt am Main, Germany*. V. *Fischer-Tropsch*. *CIOS Rept.* XXXI-23, 1945, pp. 6-18; *TOM Reel* 196; *PB Rept.* 12,624.

Research by the Lurgi organization has been concentrated on the development of a middle-pressure recycle operation, particularly with Fe catalysts. This type of operation is claimed to have the following advantages: use of a synthesis gas of CO:H<sub>2</sub> ratio 1:1; easier temperature control owing to high gas velocity through catalyst bed; increased olefin product; less C and CH<sub>4</sub> formed on the catalyst. No commercial synthesis plants using an Fe catalyst have been built in Germany, but designs had been completed for erection of a plant in Italy. Particular interest had been directed toward recycle operation of the Fischer-Tropsch process using the standard externally cooled middle-pressure reactor and a relatively low recycle ratio. A pilot-plant unit, operating for 2 yr. with a Co catalyst and a single pass, gave a yield of 155-162 gm. of liquid plus gasol/m<sup>3</sup>; increasing the recycle ratio to 3:1 increased the throughput by 30% without loss of yield or obtained a yield of 170 gm./m<sup>3</sup> at the same throughput. With the active Fe catalyst (100 Fe, 25 Cu, 9 Al<sub>2</sub>O<sub>3</sub>, 2K<sub>2</sub>O, 30 SiO<sub>2</sub>) the yield was 170 gm./m<sup>3</sup> at the normal recycle ratio. The Fe catalyst was made by dissolving Cu and Al nitrates in 10% solution of ferric nitrate in amounts that would give the specified ratio of metals, heating nearly to boiling, adding enough 10% solution of Na<sub>2</sub>CO<sub>3</sub> to precipitate the metals as hydroxides, adding kieselguhr, and washing with hot water to a pH of 8.0 and then with K<sub>2</sub>CO<sub>3</sub> solution. The nitrates must be removed completely in order to make reduction temperature control easy and positive. After complete drying, the catalyst is reduced with H<sub>2</sub> at 250°-350° for 1-4 hr., the flow rate of H<sub>2</sub> being 1 m<sup>3</sup>/kg. of catalyst/hr. Reduction with synthesis gas is possible. It is believed that the life of the catalyst would be about 1 yr. The capital cost of a new plant is stated to be \$600-900 RM./ton of liquid product/yr., although recently a quotation of 600 RM. was cited. The operating cost is given as 24 pf./kg. of product, while the most favorable income is obtained by operating for the maximum yield of hard wax at 45 pf./kg. Lurgi has built the charcoal-absorption units for nearly all of the Fischer-Tropsch plants in Germany. Charcoal absorption is believed definitely more economical than oil absorption up to 10 atm. pressure, and the latter is preferable above 15 atm. with the choice between 10 and 15 atm., depending on local conditions. A recent advance in charcoal absorption technique is the design of a plant to work at -50°, the objective being the separation of CH<sub>4</sub>. The costs are said to be slightly less than those for refrigeration.

453. ———. *Metallgesellschaft-Lurgi, Frankfurt-am-Main, Germany*. VII. *High-Pressure Gasification*. *CIOS Rept.* XXXI-23, 1945, pp. 29-42; *TOM Reel* 196; *PB Rept.* 12,624.

In the high-pressure gasification process developed by Lurgi, solid fuel, preferably weakly coking or non-coking bituminous and brown coals, is continuously

gasified at from 20-30 atm. pressure with O<sub>2</sub> and steam. The coal need not be dry, but the water content should not exceed 25%. Four plants had been built by Lurgi: At Hirschfelde, 5 million m<sup>3</sup> gas/year; 2 at Böhlen, 150 million m<sup>3</sup>; and at Bräx, 100 million m<sup>3</sup>. The generator and its operation are described, operating results are presented, and directions are given for recovery of the liquid products. Results are given for 3 kinds of fuel—2 brown and 1 lean bituminous coal. Composition of a typical purified city gas—CO<sub>2</sub>, 3.0; C<sub>2</sub>H<sub>6</sub>, 0.5; O<sub>2</sub>, 0.1; CO, 22.8; H<sub>2</sub>, 48.7; CH<sub>4</sub>, 22.6; N<sub>2</sub>, 2.3%; gas yield 760 m<sup>3</sup>/ton; O<sub>2</sub> requirement 0.15 m<sup>3</sup>/m<sup>3</sup> gas (about one-half that required by Winkler generator); efficiency of fuel conversion, about 85.2%; cost 2.4 pf./m<sup>3</sup> with brown coal at 6.5 RM./ton. In the making of synthesis gas a different procedure is followed. It has been found that the actual pressure existing in the pressure generator influences the nature of the produced gas; at lower pressures less CH<sub>4</sub> is formed in the presence of C<sub>2</sub> pressure displaces the CO:CO<sub>2</sub> equilibrium in favor of CO<sub>2</sub>. At low temperature also the equilibrium is further displaced in favor of a reduced formation of CO. Since the required reduction of CO formation is not great, it is adequate to reduce the pressure from the usual 20 atm. to about 5-10 atm. Practical tests have shown that a CO-H<sub>2</sub> gas mixture suitable for the Fischer-Tropsch synthesis with Co-ThO<sub>2</sub> catalyst can be prepared by the gasification of low-temperature bituminous coke when employing a pressure of about 5.5 atm. with both O<sub>2</sub> and steam. Under such conditions a crude gas of composition (CO<sub>2</sub>, 29.3; CO, 21.9; H<sub>2</sub>, 44.0; CH<sub>4</sub>, 3.3; N<sub>2</sub>, 1.5%) is obtained, which, after the CO<sub>2</sub> is scrubbed out, yields a synthesis gas of composition: CO<sub>2</sub>, 1.0; CO, 30.7; H<sub>2</sub>, 61.6; CH<sub>4</sub>, 4.6; N<sub>2</sub>, 2.1%. Furthermore, by increasing the addition of steam in the pressure gasification, the formation of CO may be so reduced that a scrubbed gas containing 70-75% H<sub>2</sub> and only 15% CO is produced suitable for NH<sub>3</sub> synthesis or for hydrogenation. In preparing synthesis gas of 1.2 H<sub>2</sub>:CO ratio to be used with the Fe catalyst, the procedure again is different. An analysis of the various possibilities available for the solution of the problem has led to the conclusion that economically the most advantageous method for preparing the gas from brown coal is to employ O<sub>2</sub> at a pressure of about 23.5 atm., and after scrubbing the gas to remove about 1/2 of the CO<sub>2</sub> and some of the H<sub>2</sub>S. The gas is heated to 145°, saturated with H<sub>2</sub>O, again preheated to 500°, and by partial combustion with O<sub>2</sub> heated to 1300°, in the absence of a catalyst to convert the CH<sub>4</sub> content to CO and H<sub>2</sub>. After scrubbing to remove CO<sub>2</sub> the synthesis gas has the composition: CO<sub>2</sub>, 2.0; C<sub>2</sub>H<sub>6</sub>, 0.2; CO, 42.2; H<sub>2</sub>, 50.7; CH<sub>4</sub>, 2.4; N<sub>2</sub>, 2.5%. In this method of synthesis-gas production, 0.317 m<sup>3</sup> of O<sub>2</sub> is consumed per m<sup>3</sup>. A flow sheet with diagram of apparatus is appended. O<sub>2</sub> for the process is produced by the Linde-Frankl method at a cost of 2.2-2.5 pf./N m<sup>3</sup> in units of 1,000-2,000 N m<sup>3</sup>/hr. capacity and power consumption of 0.65-0.68 kw.-hr./N m<sup>3</sup>.

CHAKRAVARTY, J. N. See abs. 1183.

454. CHAKRAVARTY, K. M. [Equilibrium Constants of the Reactions CO+3 H<sub>2</sub>=CH<sub>4</sub>+H<sub>2</sub>O; CO<sub>2</sub>+4 H<sub>2</sub>=CH<sub>4</sub>+2 H<sub>2</sub>O; and 2 CO+2 H<sub>2</sub>=CH<sub>4</sub>+CO<sub>2</sub>.] Ztschr. Elektrochem., vol. 34, 1928, pp. 22-25; Chem. Abs., vol. 22, 1928, p. 4040.

Constants for the above equilibria at temperatures 800°-1300° have been calculated: (a) From the variation with temperature of the equilibrium constants for C+2 H<sub>2</sub>=CH<sub>4</sub>; 2 CO=C+CO<sub>2</sub>; and CO+H<sub>2</sub>=CO+H<sub>2</sub>O; and (b) from the heats of reaction and the specific heats and chemical constants of reactants and products. The figures obtained are compared and discussed.

455. ———. Catalytic Reduction of Carbon Monoxide. Sci. and Culture, vol. 4, 1938, pp. 300-301; Chem. Zentrabl., 1939, I, p. 3996.

CO can be reduced at 245° by means of a Ni-Cu catalyst activated and reduced at 275° to a gas mixture, which contains more olefins (3.7%) than CH<sub>4</sub> (1.7%).

456. ———. Hydrogenation of Nickel Carbonyl. Ind. Eng. Chem., vol. 31, 1939, pp. 1059-1060; Chem. Abs., vol. 33, 1939, p. 7498.

Evidence is given to show that the principal reactions in the process of Litkenhous and Mann (see abs. 2122) are CO+H<sub>2</sub>=C+O<sub>2</sub>, and 2 CO+2 H<sub>2</sub>=CO<sub>2</sub>+CH<sub>4</sub>. (See abs. 2121.)

457. ———. Synthetic-Fuel Industry in India. Sci. and Culture, vol. 4, 1939, pp. 573-581; Chem. Abs., vol. 33, 1939, p. 5153.

Bergius, Fischer-Tropsch processes for hydrogenating coal, the preparation and use of alcohol motor fuels, compressed-fuel gases, and sewage-disposal gas, and their applications to motors are discussed with particular reference to Indian conditions. Of 103,000,000 gal. of gasoline consumed in 1937, about 15.4 million gal. was produced in India and 38.1 million gal. imported from Burma. The erection of a plant like that at Billingham, England, is recommended as a means for protecting the motor-fuel supply both in peace and war.

458. ———. Conversion of Coal Into Oil. The Fischer-Tropsch Process. Jour. Indian Chem. Soc., Ind. and News Ed., vol. 3, 1940, pp. 185-192; Chem. Abs., vol. 37, 1943, p. 4878.

Ni can replace Co in the Co-ThO<sub>2</sub> catalyst. At 1 atm. the yield of solid paraffins reaches a maximum at about 170°; that of liquefiable hydrocarbons, at 180°. Pressures greater than 15 atm. are not advantageous. Briefly reviews large-scale operation in the Ruhr.

———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. IV. Specific Nature of Promoter Effect on a Nickel Catalyst Using as Reactants Water Vapor and Equal Volumes of Carbon Monoxide and Hydrogen. See abs. 463.

———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. V. Study of the Promoter Effect on Nickel Catalyst. See abs. 464.

———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. VI. Poisoning by Carbon Deposition. See abs. 465.

See abs. 1184, 1190, 1191.

459. CHAKRAVARTY, K. M., AND CHAKRAVARTY, P. B. Effect of Potassium Carbonate on Nickel Catalysts for the Fischer-Tropsch Synthesis. Sci. and Culture, vol. 12, 1946, pp. 110-111; Chem. Abs., vol. 41, 1947, p. 1989.

Catalysts containing traces of K<sub>2</sub>CO<sub>3</sub> were found to lose their activity after passage of small volumes of H<sub>2</sub>-CO mixture. The deactivated catalyst, after being washed with distilled water and reduced at 200°, was negligibly active at first but rose in activity to a steady value somewhat below that found with the original preparation. The catalyst composition was: Kieselguhr, 46%; Ni, 45.77%; ThO<sub>2</sub>, 8.9%; and K<sub>2</sub>CO<sub>3</sub> traces. A similar preparation containing 0.0823% CeO<sub>2</sub> behaved in the same manner; the reactivated catalyst was not very active at 178°-180° but was steadily active at 219°-220°. The presence of K<sub>2</sub>CO<sub>3</sub> causes the formation of C, CO<sub>2</sub>, and H<sub>2</sub>O rather than hydrocarbons.

460. CHAKRAVARTY, K. M., AND GHOSH, J. C. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. I. Quart. Jour. Indian Chem. Soc., vol. 2, 1925, pp. 150-156; Chem. Abs., vol. 20, 1926, pp. 860-861.

Sugar charcoal-Ni catalyst for the reaction CO+3 H<sub>2</sub>=CH<sub>4</sub>+H<sub>2</sub>O retained its activity undiminished for months when the ratio H<sub>2</sub>:CO was 3:1. The critical space velocity (cm.<sup>3</sup> gas mixture per cc. catalyst per minute) below which CO disappeared was fairly great (1.3 at 300°, 1.7 at 335°, 3.6 at 358°, >4.3 at 400°). This catalyst entirely suppressed the reaction 2 CO=C+CO<sub>2</sub> and prevented deposition of C on the Ni surface. CeO<sub>2</sub> acted as a promoter for this catalyst increasing the critical space velocity at 355° from 3.5 to 4.4. Some CO<sub>2</sub>, about 9 volume % of exit gas, was produced, owing mainly to the reaction 2 CO+2 H<sub>2</sub>=CO<sub>2</sub>+CH<sub>4</sub>, and partly to the reaction C+2 H<sub>2</sub>O=CO<sub>2</sub>+2 H<sub>2</sub>.

461. ———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. II. Production of Fuel Gases Rich in Methane. Quart. Jour. Indian Chem. Soc., vol. 2, 1925, pp. 157-164; Chem. Abs., vol. 20, 1926, p. 861.

Use of sugar charcoal-pumice-Ni catalyst for the formation of CH<sub>4</sub> was studied with equimolar mixtures of H<sub>2</sub> and CO, with view to its use in enriching blue water gas (H<sub>2</sub>:49%; CO:42%). This catalyst was not as efficient as a sugar charcoal-Ni catalyst for promoting the reaction 2 CO+2 H<sub>2</sub>=CH<sub>4</sub>+CO<sub>2</sub> (I) and was little improved by addition of CeO<sub>2</sub>. Pumice-V<sub>2</sub>O<sub>5</sub>-Ni (A) was at first very effective but rapidly lost its activity; as reaction (I) was retarded, the undesirable reaction CO+3 H<sub>2</sub>=CH<sub>4</sub>+H<sub>2</sub>O (II) was favored, though with a smaller total conversion. A sugar charcoal-pumice-V<sub>2</sub>O<sub>5</sub>-Ni catalyst (B) at 400°-450° retained for months the initial activity of (A). Increasing space velocity favored reactions (II), but even with a space velocity of over 25 cc. gas per cm.<sup>3</sup> catalyst per min. only 20% of the CH<sub>4</sub> was formed by reaction (II). If sugar charcoal was replaced by coconut charcoal the catalyst deteriorated rapidly; Fe<sub>2</sub>O<sub>3</sub> in place of V<sub>2</sub>O<sub>5</sub> made (II) the chief reaction. The gas obtained by use of catalyst (B) was comparable in calorific value to carbureted water gas, though much less poisonous; removal of CO<sub>2</sub> present in amounts as great as 33%, would give a gas of very high calorific value.

462. ———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. III. Study of Various Catalysts. Quart. Jour. Indian Chem. Soc., vol. 4, 1927, pp. 431-436; Chem. Abs., vol. 22, 1928, p. 1085.

Catalysts as follows were investigated at 300° on asbestos: Ni(OH)<sub>2</sub>, Ni(OH), and Mn(OH)<sub>2</sub>, Ni(OH)<sub>2</sub>, on Mn(OH)<sub>2</sub>, MnO, on Ni(OH)<sub>2</sub>, Ni(OH)<sub>2</sub>, and Mg(OH)<sub>2</sub>, Ni(OH)<sub>2</sub>, on Mg(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, on Ni(OH)<sub>2</sub>, Ni(OH)<sub>2</sub>, and Zn(OH)<sub>2</sub>, Ni(OH)<sub>2</sub>, on Zn(OH)<sub>2</sub>, Ni(OH)<sub>2</sub>, and Pb(OH)<sub>2</sub>, NiHVO, on Ni(OH)<sub>2</sub>, Cr(OAc)<sub>3</sub>, on Ni(OH)<sub>2</sub>, (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>, on Ni(OH)<sub>2</sub>, Ni(OH)<sub>2</sub>, and Al(OH)<sub>3</sub>, Ni(OH)<sub>2</sub>, on Al(OH)<sub>3</sub>, Al(OH)<sub>3</sub>, on Ni(OH)<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, on Al(OH)<sub>3</sub>. Those with Al were most promising. A rapid fall of activity occurred in all cases. The pumice-sugar carbon-Ni catalyst at 400° did not show marked increase of activity with Ni about 10:2:0.65. Loss of activity was slow, but C always deposited on the catalyst.

463. CHAKRAVARTY, K. M. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. IV. Specific Nature of Promoter Effect on a Nickel Catalyst Using as Reactants Water Vapor and Equal Volumes of Carbon Monoxide and Hydrogen. Science and Culture, vol. 3, 1938, p. 399; Ztschr. anorg. Chem., vol. 237, 1938, pp. 381-387; Chem. Abs., vol. 32, 1938, pp. 2818, 6535.

Apart from CH<sub>4</sub> formation a C-Ni catalyst containing thorium and ceria accelerates the formation of CO, CO<sub>2</sub>, and H<sub>2</sub> from H<sub>2</sub>O and C, but with K<sub>2</sub>CO<sub>3</sub> the formation of C and CO<sub>2</sub> from CO is promoted. The addition of a small quantity of a mixture of Ce nitrate

and NH<sub>3</sub> vanadate or of Ce nitrate and Cr(OAc)<sub>3</sub> to the Ni(OAc)<sub>2</sub> used in preparing the catalyst brings about a more complete reduction of the Ni at 300°. The formation of CO<sub>2</sub> and CH<sub>4</sub> is indirectly helped by them. The thorium-ceria mixture increases the uniformity of the Ni particles, prevents granule formation on the surface and clogging of the pores of the pumice used, and prevents sintering. At 400°-450° the Ni catalysts adsorb much CO<sub>2</sub>.

464. ———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. V. Study of the Promoter Effect on Nickel Catalyst. Jour. Indian Chem. Soc., vol. 15, 1938, pp. 245-248; Chem. Abs., vol. 32, 1938, p. 8742.

Reduction of Ni catalyst at a temperature of 300° is incomplete when it is prepared from pure Ni acetate. Addition of a small quantity of a mixture of Ce nitrate and NH<sub>3</sub> vanadate or of Ce nitrate and Cr acetate helps in bringing about a more thorough reduction. Thus catalysis of a reaction 2CO+2H<sub>2</sub>=CO<sub>2</sub>+CH<sub>4</sub> is accelerated by these promoters through their influence on the preparation of the Ni. Whether the promoters have a direct effect on the reaction has not been settled.

465. ———. Catalytic Formation of Methane From Carbon Monoxide and Hydrogen. VI. Poisoning by Carbon Deposition. Jour. Indian Chem. Soc., vol. 16, 1939, pp. 663-670; Chem. Zentrabl., 1940, II, p. 723; Chem. Abs., vol. 34, 1940, p. 4723.

Deposited C may be adsorbed on Ni particles or may form a simple layer on the surface. Moreover, Ni may undergo carbide formation and Ni<sub>3</sub>C may have catalytic activity. It has been shown that the reaction 2CO=C+CO<sub>2</sub> is catalyzed by Ni and also by Ni<sub>3</sub>C. The reaction CO+3H<sub>2</sub>=CH<sub>4</sub>+H<sub>2</sub>O is 2.50, Cu 0-1.50, Mg 0.70-1.30, Si 0.10-0.35, and Fe 0.10-0.50%. Al is the remainder, but so that if Cu is near its maximum, the total of the Ni, Sb, and Si is near the lower limit and vice versa. The alloy may also contain Mn up to 0.25%.

466. CHAKRAVARTY, K. M., AND SARKER, J. M. Catalytic Formation of CH<sub>4</sub> From CO and H<sub>2</sub>—A Study of Ni and Ni-Alumina Catalysts Prepared From the Hydroxide, Using KOH, NaOH and NH<sub>4</sub>OH as Precipitants. Current Sci., vol. 13, 1944, p. 127; Chem. Abs., vol. 38, 1944, p. 6178.

In a mixture of CO, H<sub>2</sub>, and H<sub>2</sub>O, roughly 1:1:1, 2 reactions occur in the presence of Ni catalysts: (1) 2CO+2H<sub>2</sub>=CH<sub>4</sub>+CO<sub>2</sub>. (2) CO+H<sub>2</sub>O=CO<sub>2</sub>+H<sub>2</sub>. The influence of KOH, NaOH, and NH<sub>4</sub>OH, used to precipitate Ni, was small. Alumina promotes reaction (1); its maximum activity occurs at a concentration below 0.10%. Addition of K<sub>2</sub>CO<sub>3</sub> to the catalyst promotes reaction (2). Results of 11 runs are tabulated, with analyses of reactants and resultants, weight and volume of catalyst, rate of flow and total volume of gases, and reaction temperatures.

467. CHAKRAVARTY, K. M., AND SEN, R. X-Ray Diffraction Studies of a Nickel-Thoria-Kieselguhr Catalyst for Fischer-Tropsch Synthesis. Nature, vol. 160, 1947, pp. 907-908; British Abs., 1948, A L, p. 155.

The presence of a few diffraction lines of kieselguhr on the X-ray diffraction diagram shows that, in the process of depositing Ni on kieselguhr, the structure has undergone a change. The 2 lines of the kieselguhr shown in the photograph are identified as the strong lines of ferric oxide present in the kieselguhr. The lines of silica of the kieselguhr are absent in that of the catalyst. It is concluded from this that during deposition of metallic Ni and Th on the kieselguhr the crystalline portion of silica becomes amorphous, while the structure and the crystallinity of the ferric oxide remain unchanged. The broadness of the lines indicates,

however, that the crystal particles of ferric oxide have disintegrated, yielding crystallites of smaller size. The change in structure was brought about, not by the heating of the kieselguhr in  $H_2$  during the deposition of Ni and Th, but by the disintegration caused by the decomposition of the carbonates of Ni and Th deposited as an initial step in the preparation of the catalyst. Ni is present as is Th in crystalline form in these samples.

CHAKRAVARTY, P. B. See abs. 459.

468. CHAO, T. Y., Hsu, W. W., and WEN, C. [Study of Iron Catalysts for the Synthesis of Liquid Fuels From Carbon Monoxide and Hydrogen.] Jour. Chinese Chem. Soc., vol. 12, 1945, pp. 1-14; Chem. Abs., vol. 40, 1946, p. 3865.

Because of the limited supply of Co and Ni in China, increased use must be made of Fe catalysts in industrial processes. In preparing the catalyst, Fe plus varying amounts of Cu as promoter are dissolved in  $HNO_3$ , mixed with starch, kieselguhr, and  $K_2CO_3$ , and ignited. Water gas is passed through the reactor at a rate of 2.1 per hr. and the yield measured in terms of ml. per m.<sup>2</sup> of gas. Each run was continued for 20 days or more, and the products were examined at 24-hr. intervals. Maximum results are obtained when about 0.5% of  $K_2CO_3$  is present and when the Fe:Cu ratio is 5:1. Satisfactory yields are obtained at a reaction temperature of 240°. The activity of the Fe catalysts was long lived. The kogasins produced gave on distillation good yields of light oil as well as paraffin.

469. CHAPMAN, O. L. Synthetic Liquid Fuels. 1949 Annual Report of the Secretary of the Interior. I. Oil From Coal. II. Oil From Oil Shale. III. Liquid Fuels From Agricultural Residues. IV. Oil From Secondary Recovery and Refining. Bureau of Mines Repts. of Investigations 4631, 4652, 4653, 4654. February 1950, pp. 1-xxii, 1-62, 1-70, 1-13, and 1-26.

Many technical problems are yet to be solved in placing liquid fuels from oil shale and coal on a competitive basis with petroleum fuels. Developments are now centered on operation rather than on design and construction of laboratories and demonstration plants, and process improvements should effect a reduction in operating costs and thus the establishment of a synthetic liquid fuels industry from domestic resources at reasonable rates. The estimated capital investment for a crude shale-oil plant (10,000 bbl. per day) is \$4,138 per bbl. and for a coal-hydrogenation plant (30,000 bbl. per day) \$8,227 per bbl. Actual production costs per gal. of gasoline are estimated at \$0.073 and \$0.103, respectively, or allowing for a 6% profit on average unamortized capital investment, \$0.09 and \$0.145. It would thus appear that oil-shale processing is not far from the point of commercial utilization. The cost of shale mining has recently been reduced to \$0.29 per ton. It is conceded, however, that it is doubtful at present that a coal-hydrogenation plant producing motor gasoline would be an attractive commercial investment in view of the above costs. It is reasonable to expect that these costs can be reduced by the new developments in catalysts and operating methods under investigation, perhaps by 15-20%. Cost calculations for commercial gas-synthesis operations using coal will be based on the demonstration tests as carried out at the plant being erected at Louisiana, Mo. It will be about a year before these estimates can be made. Several gasification processes for the production of synthesis gas from coal are in the pilot-plant stage. These investigations are of prime importance, since the cost of synthesis gas will always be a large fraction (50-70%) of the cost of liquid fuels from the gas-synthesis process. (Lengthy abstract appears in Chem. Eng. News, vol. 28, pp. 914, 916.)

470. ———. Synthetic Liquid Fuels. 1950 Annual Report of the Secretary of the Interior. I. Oil From Coal. II. Oil From Oil Shale. III. Liquid Fuels From Agricultural Residues. IV. Oil From Secondary Recovery and Refining. Bureau of Mines Repts. of Investigations 4770, 4771, 4772, 4773, February 1951, pp. i-xiv, 1-74, 1-88, 1-12, 1-16.

Review of operations during 1950 of the synthetic liquid fuels laboratories and demonstration plants. Progress in the oil-shale development program reveals the commercial feasibility of these operations, and it is believed that gasoline and oil can be produced from shale at costs that compete favorably with those for petroleum products. The estimated cost of delivering raw shale to the retorting plant, exclusive of depletion, interest, and profits, is \$0.426/ton or \$0.015/gal. of shale oil. The retorting process has been improved as to both method and cost by the development of the gas-combustion retort. New experience has been gained in the operation of the coal-hydrogenation demonstration plant. Costs are being reestimated and will be reported on completion. It appears that the cost of producing gasoline from coal is somewhat greater than it is from shale. The potentialities of the production of aromatic chemicals, such as benzene and phenols, are being investigated. The great flexibility in the operation of coal-hydrogenation plants to produce different grades and types of fuels is of great strategic advantage. The construction of one or more commercial plants is also recommended. The gas-synthesis process for the production of synthetic liquid fuels from coal by way of synthesis gas ( $CO+H_2$ ) is to be placed in operation at the demonstration plant at Louisiana, Mo. Studies of this process are not as far advanced as those for coal hydrogenation or oil shale. The greatest attention is being given to the completion of a method for the production of synthesis gas by gasifying pulverized coal in the presence of steam and  $O_2$  under pressure of 450 p. s. i. The process is highly promising and preliminary cost studies have indicated that it should reduce considerably the cost of synthesis gas. Commercialization of the gas-synthesis process awaits completion of the present studies and results of the demonstration work. Other projects under investigation are: Vortex reactor for coal gasification, underground gasification, purification of synthesis gas, and the Oxo process.

471. CHAPMAN, D. L., and HOLT, A. Synthesis of Formaldehyde. Jour. Chem. Soc., vol. 87, 1905, pp. 916-920.

By passing  $CO$  and  $H_2$  over Ni wool heated to 480°-500°, amounts of  $CH_2O$  were obtained that could be detected only by the most careful tests with Schiff's reagent. With  $CO$ , and  $H_2$  and with  $CO, H_2$ , and steam appreciable quantities of  $CH_2O$  were obtained.

472. CHARPY, G., and PINGAULT, P. [Conditions Required for Formation of Cementite.] Compt. rend., vol. 187, 1928, pp. 554-556; Chem. Abs., vol. 23, 1929, p. 79.

Review of previous experiments, showing that Fe could be carburized at 600°-650° with the formation of a layer of cementite separated from the original metal by a narrow transition zone and that cementite could decompose at 700°. Pure electrolytic Fe filings, free from H, were carburized by cyanide or hydrocarbons, and the physical properties were studied. The density, decreased gradually with absorption of C to a limit of 7.40 at 0°. The magnetic attraction of 1 gm. of Fe filings decreased, on carburizing, from 7 gm. to a constant value of about 4 gm. The filings carburized to constant density and magnetic attraction contained 6.75% C and left no trace of insoluble C when dissolved in  $HNO_3$ . This product did not suffer

any change in properties after gradual heating to 1,000° during 10 hr. Slight separation of graphite in previous experiments of this nature may be attributed to oxidation. Fine Fe wire was transformed entirely into cementite, with no trace of graphite, after heating to 850° in cyanide. Pyrometer protection tubes of Fe 1 mm. thick from cementation furnaces were also found to be completely transformed into cementite. Carburization of solid Fe below 1,000° tends therefore to form cementite, and the distribution of the C beneath the surface is determined only by the rate of solution and diffusion of cementite in solid Fe.

473. CHARRIN, V. [Synthetic Fuels.] Chaleur et ind., vol. 10, 1929, p. 380; Chem. Abs., vol. 24, 1930, p. 1197.

Brief mention is made of some French workers, Marcelin Berthelot, Sabatier and Senderens, Prudhomme and Houdry. The Pieters furnace at Millau and the Tauzer furnace at Lalque, France, have not given the expected results. An attempt is being made to use the Prudhomme-Houdry process in the catalytic hydrogenation of the water gas from St. Julien lignite to produce a motor spirit.

474. CHASHNIK, L. M. [Synthesis of Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 360-369; Chem. Abs., vol. 29, 1935, p. 7393.

Mathematical equations are derived for the calculation in general form of the equilibrium concentration of  $MeOH$  for the maximum productivity of the apparatus, and for connecting the ratio  $H_2 : CO$  in the freshly introduced gas with that in the circulating gas. The presence of inert gas strongly affects the yield of  $MeOH$ , while a change in the ratio  $H_2 : CO$  has relatively little effect.

CHATTERJEE, B. See abs. 166a.

475. CHAUDRON, G. [Reversible Reactions of Carbon Monoxide on the Oxides of Iron.] Compt. rend., vol. 172, 1921, pp. 152-155; Jour. Chem. Soc., 1921, II, p. 178.

Starting with  $Fe_2O_3$  and  $CO$ , the equilibrium is studied over a temperature range of 300°-1,000°. The  $Fe_2O_3$  is reduced to the magnetic oxide, and beyond this stage 2 reactions may occur. Below 580° there is a single system corresponding with  $Fe_2O_3 + 4CO = 4CO_2 + 3Fe$ . Above 580° there are 2 equilibria before arriving at Fe, namely,  $Fe_2O_3 + CO = 3FeO + CO_2$  and  $FeO + CO = Fe + CO_2$ . The 3 solid phases coexist in equilibrium at 580°. Below 580°  $FeO$  is unstable and is transformed into a mixture of Fe and the magnetic oxide,  $4FeO = Fe_3O_4 + Fe$ .

476. ———. [Reversible Reactions of Hydrogen and Carbon Monoxide on Metallic Oxides.] Ann. chim., vol. 16, 1921, pp. 221-281; Chem. Abs., vol. 16, 1922, pp. 212-213.

Apparatus combined features previously used with modifications designed to effect continuous slow circulation of the gas phase over the solid phases and to require a single thermostat well removed from the furnace. The composition of the gas phase was determined at intervals, pH O-pH by tension measurements  $C_{CO}-C_{CO_2}$ , by refraction with an interferential method shown to be capable of detecting a variation of 0.5% in composition. Equilibrium was determined by both oxidation and reduction experiments. The triple point at which Fe, FeO, and  $Fe_3O_4$  coexist was found to be 570°, the data being concordant for both gas phases. Above 570° the equilibrium curve has 2 branches corresponding to  $Fe + H_2O = FeO + H_2$  (and  $Fe + CO = FeO + CO$ ) and  $3FeO + H_2O(CO_2) = Fe_3O_4 + H_2(CO)$ . Below 570° 1 system only exists:  $3Fe + 4H_2O(CO_2) = Fe_3O_4 + 4H_2(CO)$ . The triple point corresponds to the invariant system  $4FeO = Fe_3O_4 + Fe$ . This transformation was directly observed by main-

taining below 570°  $FeO$  prepared at high temperature, 900°, and using metallographic methods and appearance of ferromagnetic properties. The diagram, temperature-gas composition, fixes the conditions for preparing Fe, FeO, and  $Fe_3O_4$ . The following equilibria were also studied:  $Co + H_2O = CoO + H_2$ ;  $Mo + 2H_2O = MoO_3 + 2H_2$ ;  $W + 2H_2O = WO_3 + 2H_2$ ;  $2WO_3 + H_2O = W_2O_7 + H_2$ . The last confirm the existence of the oxides  $WO_3$  and  $W_2O_7$ , and the diagram fixes the conditions for preparing  $WO_3$ . Ni, MnO, and  $UO_2$  are not oxidized by water vapor. From the measurements of the systems  $Fe + H_2O(CO_2) = FeO + H_2(CO)$  values of the water-gas equilibrium  $K = (C_{CO}C_{H_2O} - C_{CO_2}C_H)$ , are calculated for 686°, 786°, 886°, and 986° in excellent agreement with Haber's values. For  $K=1$  was found 810°; Haber, 825°.

477. ———. [Reduction of Metallic Oxides by Means of Hydrogen and Carbon Monoxide.] Chim. et ind., vol. 8, 1922, pp. 959-964; Chem. Abs., vol. 17, 1923, p. 521.

Review of the mechanics of the reversible reactions  $Fe + H_2O = FeO + H_2$  and  $Fe + CO = FeO + CO$  and their relation to the dissociation of  $FeO, H_2O$ , and  $CO_2$ , and application of these results to the measurement of the equilibrium of a mixture of  $CO$  and  $CO_2$ .

See abs. 1053, 1054, 1514, 2272, 2275.

478. CHAUDRON, G., and BÉNARD, J. [Process of Decomposition of Ferrous Oxide.] Bull. soc. chim. France, 1949, D, pp. 117-119; Chem. Abs., vol. 43, 1949, p. 6901.

Decomposition of  $FeO$  at 300°-570° is exclusively a solid-phase reaction. The reaction was followed by thermomagnetic analysis. A phase diagram is given for the system  $FeO-Fe_3O_4-Fe$ . The rate of decomposition was determined to be a function of the temperature of preparation, the concentration of  $O_2$  during preparation, and the presence of particles of Fe or  $Fe_3O_4$ .

479. CHAUDRON, G., and FORESTIER, H. [Decomposition of Ferrous Oxide. Anomalies of Dilatation Relative to Its Instability.] Compt. rend., vol. 178, 1924, pp. 2173-2176; Chem. Abs., vol. 18, 1924, p. 3306.

Object was to study the velocities of 2 reactions involved in the equilibrium  $4FeO = Fe_3O_4 + Fe$ .  $FeO$  was prepared at 800°-900° and cooled rapidly to avoid decomposition. It was then heated in a vacuum for 24 hr. at constant temperature and analyzed by treating with dilute  $CuSO_4$  for 12 hr. Titration with  $KMnO_4$  gave the weight of Fe that entered the solution. The fraction of the  $FeO$  transformed in 24 hr. was plotted against the temperature. At 300° free Fe could be determined. The fraction transformed then increased to 80% at 480°, passing through a maximum there and falling to 0% at 570°. At 592° 24% of  $FeO$  and at 600° 51% of  $FeO$  were formed in 24 hr. from a sample originally containing 20% of  $FeO$ . At 445° the velocity of the reaction is expressed by  $dx/dt = k(100-x)^2$ . When change in volume is plotted against temperature, anomalies are observed corresponding to the chemical changes.

CHAUKAVIN, M. K. See abs. 2754.

480. CHAUX, R. [Combustible Liquids From Coal—A Lecture Delivered at the College of France.] Bull. soc. chim., vol. 43, 1928, pp. 388-411; Chem. Abs., vol. 22, 1928, p. 2826.

Review of production of combustible liquids from coal by hydrogenation and by utilizing hydrocarbon constituents of coke-oven gas for producing alcohols and using coal tars for producing  $C_2H_4$ , its homologs, and other aromatic compounds. The syntheses of  $MeOH$ , synthol and liquid hydrocarbons from  $CO$  pro-

duced by the gasification of coal are discussed. Bibliography of 160 refs.

481. CHEMICAL AGE. Latest German Developments in Coal Liquefaction. Vol. 13, 1925, pp. 268-269.

Information on processes for coal liquefaction, the Bergius process, and a brief discussion of the possibilities of synthol.

482. ———. Fischer Process. Vol. 35, 1936, p. 367. Editorial comments on Melchert address by F. Fischer to the Institute of Fuel.

483. ———. Gasoline From Water Gas, Germany. Vol. 36, 1937, p. 152.

Loan of RM 55,000,000 for Gelsenberg Benzin A.-G. was oversubscribed on February 4, first application day. The loan is guaranteed by a mortgage over the Gelsenberg's future plant, while the debt-service security is reinforced by a guarantee of Vereinigte Stahlwerke. When production starts, Gelsenberg will, with Leuna-werke, another subsidiary of Vereinigte Stahlwerke, be the largest hydrogenation works in Germany. But where Leuna-werke uses lignite as raw material and proceeds by the costly Bergius process, depending on high-temperature pressures, involving rapid wear and tear of plant, Gelsenberg will start from coal by using the Fischer-Tropsch process, which deteriorates the plant far less and produces higher petroleum yield with very little waste.

484. ———. Hope Long Deferred. Vol. 37, 1937, p. 267.

Editorial calling attention to possible misleading statements that have been published in the official report of the committee appointed in 1937 by the Australian Government to advise upon the economics of establishing a hydrogenation plant in Australia. The committee has announced the conclusion that if interest on capital is charged at 3½% and 15 yrs. is allowed for amortization, the total cost of hydrogenated gasoline from bituminous coal will be 13.8 d. per imperial gal. If, following the Imperial Chemical Industries practice, the interest is charged at 6% and amortization is effected in 10 yrs. the cost of the gasoline is as high as 17.3 d. per gal. The operating costs, inclusive of coal at 14s.6d. per ton, are estimated as 8.4d. per gal. Admittedly, Australian costs are higher than English costs, but the committee has calculated that under English conditions the figures for total costs would be respectively 10.5 d. per gal. and 12.75 d. per gal. These figures appear high. It has been stated in certain interested quarters that the committee's report establishes the fact that the capital cost of a Fischer-Tropsch plant is not lower than that of a hydrogenation plant for the same output. The committee found that the cost of building a Fischer-Tropsch plant would be about £100 per ton of output per yr., while that for hydrogenation would be only £73 per ton per yr. The estimates we have ourselves had the privilege of examining would show a very different picture for the Fischer-Tropsch plant. We should much like to know upon what basis the Australian figure was determined. The investigators state that they were last in Europe in 1936, when only a small experimental Fischer-Tropsch plant was in operation, and the investigators admit that it was not possible for them to obtain any costs of operation or, presumably, of erection. It would be very unfortunate if the opinions expressed in this report were allowed to influence those who are considering the inception of a chemical industry in this country based on the production of hydrocarbons by the Fischer-Tropsch process. This process can be operated in much smaller units than the hydrogenation process and with a much less highly trained staff. It would be possible to situate these plants throughout the country at collieries possessing coking coal and thus bring into being another and widespread chemical industry.

485. ———. Oil From Coal in South Africa. Vol. 36, 1937, p. 215.

A Fischer-Tropsch plant is to be erected in South Africa by the Anglo-Transvaal Consolidated Investment Co., Ltd., which has acquired the rights. This will be the first Fischer-Tropsch gasoline plant in the British Empire.

486. ———. Catalysts for the Fischer-Tropsch Process. Vol. 39, 1938, p. 391.

Fischer-Tropsch process of synthesizing petrol from CO and H<sub>2</sub> is finding its way into large-scale industry in the Far East. The Mitsui Mining Co., which has acquired the rights for the system in the Far East, is building a plant capable of producing 30,000 kl. of petrol per yr. and the South Manchurian Oil Liquefaction Engineering Co., which was founded jointly by the Mitsui Co. and the Government of Manchukuo, is also to utilize the same process in a factory to be built at Fushin. The latter, when fully equipped, will produce 100,000 kl. per yr.

Success of these enterprises naturally depends in a large measure upon the efficiency and economy of the catalyst employed. The two firms are not likely to use the catalyst discovered and recommended by Fischer himself, which is Ni containing oxides of Mn and Al as promoters and kieselguhr as carrier; but they will probably use one of those discovered in this country, such as those discovered by Dr. Genitsu Kita, Professor in the Kyoto Imperial University, and the Fuel Research Institute of the Ministry of Commerce and Industry.

Dr. Kita prepared a large range of Co catalysts containing Cu and the oxides of Th, U, and Mn as promoters, and kaolin or kieselguhr as carrier, and discovered that the oxides of U and Th were the most efficient promoters and kieselguhr the best carrier. A grade, which was made of 80% Co, 10% Cu, 2.5% ThO<sub>2</sub>, 0.5% UO<sub>2</sub>, and the balance kieselguhr gave the highest yield, 144 cc. of petrol from 1 m.<sup>3</sup> of synthesis gas. His experiment with Ni, however, was not wholly successful. He concluded that the petrol yield could not be raised, at least to such an extent that it might be compared with the yields of other catalysts unless the metal was treated by complicated methods, which would make its commercial application difficult.

Catalysts of Ni, Co, Al, and Si had their own advantages, yet all failed to yield a large enough quantity of petrol. Finally, Dr. Kita discovered that a Ni-Co catalyst prepared by precipitation methods was the most efficient and economical agent for the petrol synthesis. This catalyst of 50 parts by weight of Co, 50 of Ni, 15 of Mn, 3 of ThO<sub>2</sub>, 5 of UO<sub>2</sub>, and 125 of kieselguhr was reduced with H<sub>2</sub> for 4 hours at 400° C. When the synthesis was conducted at 190° C., it produced 166 cc. of petrol from 1 m.<sup>3</sup> of gas treated. A further study is to be made of the means of producing this catalyst at as low a cost as possible.

The Fuel Research Institute of the Ministry of Commerce and Industry has experimented with virtually all the catalysts made of Ni, Co, and other metals suggested by Japanese and foreign chemists. As a result Tsutsumi reported that a Ni catalyst containing 20% Mn, 8% UO<sub>2</sub>, and 4% ThO<sub>2</sub> is the best material, yielding 168.8 cc. of petrol per m.<sup>3</sup> synthesis gas. The reaction is carried out at 200° C. and a gas flow of 6 l. per hr.

487. ———. Oil From Coal. Vol. 39, 1938, pp. 51-52; Bull. Imp. Inst., vol. 36, No. 2, 1938.

Summary of the development of the Fischer-Tropsch process.

488. ———. Butter From Coal. Vol. 54, 1946, pp. 602-603.

The Imhausen plant at Witten, Germany, has stepped-up the operation of making butter from paraf-

fin to 350 tons per mo. The paraffin is first oxidized and then heated to extract the fatty acids, which are used to make butter or soap. For butter, the fatty acid is redistilled and glycerin and carotin are added. From 100 tons of paraffin, 80 tons of fatty acids are produced, enough to make 40 tons of butter or soap. For soap, the fatty acids are not redistilled, but soda is added. The butter produced by the Imhausen method, which contains no acetone, is the only butter that can be eaten safely by diabetics.

489. ———. Coal-Chemical Transformation. Vol. 55, 1946, pp. 725-726; Coke Smokeless-Fuel Age, vol. 8, 1946, pp. 258-260.

Now that investigation of the German chemical industry has been completed, a clearer analysis of German scientific progress and development can be made. As regards the Fischer-Tropsch process, around which almost fabulous hopes and expectations had been built, the sober truth is that the vaunted German scientific ability has produced almost nothing that was not known before the war and the impression now created upon our minds is that the commercial position of the Fischer-Tropsch synthesis is much the same after the war as it was when the war started. The possibilities and the methods for making most of the transformations from coal and gas into fuels and chemicals were known before the war, and the interim research developments do not appear to have contributed greatly to improvement in the efficiency of the Fischer-Tropsch plants or to reduction in the cost of production. To make the future of the process commercially and economically practical, the process must first be cheapened, and then a study must be made to discover in what direction it should be developed. As a method for producing fuels from coal, the process is hopelessly expensive under British conditions, since the production cost, it is calculated, would be about 2s. or 2s.6d./gal. of gasoline, a condition that cannot improve because of the rising trend in the price of coal. Further research, which would enable a high proportion of the products to be utilized as high-priced chemical products, would materially improve the economic prospects of the process. For real economic improvement, however, a reduction in the cost of the synthesis gas is needed, and it must be produced from products that would otherwise be wasted, such as natural gas or refinery cracking gas. The discovery of a catalyst not susceptible to poisoning by S would also be a useful improvement.

490. ———. Synthetic Soap and Edible Fats. Vol. 54, 1946, p. 308.

Naturally occurring animal and vegetable oils and fats, which form the normal source of soap and edible fats, are glycerides of straight-chain carboxylic acids containing an even number of C atoms in the molecule. The Fischer-Tropsch process provides a means of preparing hydrocarbons with such characteristics predominating, and these products, obtained under suitable temperatures and pressure, are a source of a wide range of aliphatic chemicals, including fatty acids of the type required for soap and edible fat preparation. The maximum production of such acids from the Fischer-Tropsch soft wax by catalytic oxidation was about 40,000 tons/yr. in Germany. About 1,800 tons/yr., of edible fat were produced by reaction of the acids with glycerin, synthesized from propylene. There was a total plant capacity for synthetic margarine production of about 7,000 tons/yr. The synthetic soap had excellent lathering properties but left an unpleasant odor on the skin. The synthetic edible fat was quite satisfactory in respect to taste and odor and was assimilated and utilized by the body in the normal manner, although the long-term effect is not yet known. It had better keeping qualities than the natural product and was utilized particularly in the food sup-

ply in submarines. Its production, however, is not economical since, under the best conditions, the production of 1 ton of synthetic soap or fat required consumption of 60-70 tons of coal.

491. ———. German Fatty Acids. Production From Lignite. Vol. 57, 1947, p. 542.

The production of fatty acids by I. G. at Oppau, in general, similar to that by the Deutsche Fettsäure Werke at Witten-Ruhr, except that the latter worked with the Fischer Gatsch paraffins, while Riebeck paraffins were used at Oppau. The latter were obtained from lignite pitch and TTH-paraffin, resulting from high-temperature hydrogenation of lignite, as well as from synthetic paraffins obtained by the Fischer-Tropsch synthesis. Output of synthetic fatty acids since 1937 amounted to 20,000 tons annually at Oppau, while Witten-Ruhr turned out double the amount. The end products were mainly used in the manufacture of soap; only a few tons were used in experiments on the manufacture of margarine. The price depended chiefly on that of the paraffins used. During the war, Oppau produced fatty acids at 2 RM per kg. or twice that of fatty acids derived from natural fats. After oxidation with air in presence of potassium permanganate, the fatty acids were distilled into 4 fractions and a residue, the latter being used for the manufacture of stove enamels, synthetic vaseline, etc.

492. ———. Utilization of Coal. Vol. 57, 1947, pp. 69-70.

Editorial comments on the economic possibility in Britain of using coal as the raw material for production of gasoline. The opinion is expressed that such utilization cannot be economical under British conditions; rather, encouragement should be given only to the use of coal for the manufacture of those products that have an export value and at the same time consume comparatively little coal in manufacture. It appears, therefore, to be more profitable from the British viewpoint to continue to import gasoline and to use the coal supplies to build up a valuable export trade and leave the production of synthetic gasoline by the Fischer-Tropsch and hydrogenation reactions to the United States where more favorable conditions exist because of the extensive supplies of natural gas and the development of the fluid catalyst.

493. ———. Fischer-Tropsch Research—Tracer Investigation. Vol. 58, 1948, pp. 680-681.

The research project, conducted by the Gulf Oil Corp., of Pittsburgh, Pa., at Mellon Research Institute using radioactive isotopes, has possibilities of improving and perhaps greatly altering the future commercial development of the gas synthesis process by further improving the conversion methods. The research method is the so-called "tracer" system which involves, in this case, the use of radioactive atoms (C<sub>14</sub>), which are chemically identical with C but which emit electrons that can be detected by the Geiger counter at any point in the reaction and thus indicate the exact course that the reaction is taking. It is hoped to prove whether the gasoline produced by the Fischer-Tropsch synthesis comes from the reaction of H<sub>2</sub> with the metal carbides formed from CO and the metal catalyst or from some other source not involving carbide formation. In the method employed radioactive C is supplied as BaCO<sub>3</sub>. Acid treatment releases radioactive CO, and from this is produced the desired radioactive CO by exposing a mixture of the CO<sub>2</sub> with ordinary CO to an incandescent tungsten filament. This radioactive CO is then reacted with an Fe catalyst to form carbide-containing radiocarbon. The hydrocarbon products derived from passage of ordinary synthesis gas (CO+2H<sub>2</sub>) over this catalyst will show no radioactivity if they are derived entirely from ordinary CO gas rather than from reduction of the Fe carbide.

If they are derived from reduction of the Fe carbide, they will show a radioactivity comparable to that of the surface of the Fe carbide catalyst. The C<sub>1</sub> experiments at about 250° F. show that the hydrocarbon gas formed has less than 10% of the radioactivity it would have if the entire surface of the catalyst reacted entirely through the mechanism of alternate carbide reduction formation.

494. ———. Dismantling of German Plants Canceled. Vol. 61, 1949, p. 799.

Synthetic fuel and rubber plants removed from the dismantling list are those of Bayer at Leverkusen; Chemische Werke Huels; Gelsenberg Benzine A.-G.; Hydrierwerke Scholven A.-G., Gelsenkirchen-Buer; Ruhrroel A.-G., Bottrop; Ruhrchemie A.-G., Oberhausen-Hoiten; Gewerkschaft Viktor, Castrop-Rauxel; Krupp-Treibstoff-Werke, Wanne-Eickel; Steinkohlenbergwerk Rheinpreussen, Moers; Dortmund Paraffin-Werke Dortmund; and Chemische Werke, Essener Steinkohle, Bergkamen. The synthetic fuel plants of Gewerkschaft Viktor and Krupp-Treibstoff-Werke, which were to close down by the end of the year, are still in operation. The German interests expect that it is only a matter of time before the synthetic and hydrogenation plants will be permitted to resume production.

495. ———. Economics of Coal Gasification. Vol. 61, 1949, p. 111.

Some operating results on the new continuous coal gasifier at Louisiana are presented. A 4-hr. full-scale test was made with gasifier temperatures averaging about 2,200° F. The feed rates were coal 2,300 lb. per hr., O<sub>2</sub> 17,000 std. cu. ft. per hr., and steam 2,000 lb. per hr. Approximately 70,000 std. cu. ft. of gas per hr. was made. The gas was 42% H<sub>2</sub>, 37% CO, 16% CO<sub>2</sub>, 4% N<sub>2</sub>, and 1% miscellaneous. It is expected that, with continuous operation, the CO<sub>2</sub> content will be reduced and a better synthesis gas obtained.

496. ———. Reshaping German Industry. Vol. 61, 1949, pp. 377-378.

Editorial presenting some arguments for and against the dismantling of the German Fischer-Tropsch and Bergius plants and the effect that it will have on German economic prospects.

497. ———. United States Coal Gasification. Vol. 60, 1949, pp. 924-925.

The production of synthetic liquid fuel occurs in 4 distinct phases: Coal gasification; gas purification; hydrocarbon synthesis; and refining of products. Each of these receives brief description, the first by aid of a sectional diagram of the Koppers O<sub>2</sub> steam gasifier. Hydrocarbons are synthesized from synthesis gas either in a unit known as an internally cooled converter, through which cooling oil is circulated, or in a slurry type reactor, the Lamo process, in which the fluidized catalyst is kept suspended in the cooling oil by internal circulation. All 4 phases represent a very advanced stage in instrumentation and automatic control.

498. ———. British and German Chemists Conference. Vol. 62, 1950, pp. 895-896.

Allied High Commission has approved the German proposals for the conversion of the Krupp-Treibstoffwerk plant at Wanne-Eickel to the production of higher alcohols by the OxyI synthesis process of Ruhrchemie A.-G. The required catalysts will be made by Ruhrchemie A.-G. Krupp-Treibstoffwerk plans to produce a number of products, such as solvents, plasticizers, and auxiliary products for the detergent industry. The German proposals also provided for conversion of the Chemischewerk Bergkamen, the Fischer-Tropsch plant of Essener Steinkohle A.-G. It had been suggested that operations for the purification of coke-oven gases and removal of poisonous substances could be carried out there, but this suggestion has not been sanctioned. The

cases of Gewerkschaft Victor, Castrop-Rauxel, which was converted to the production of nitrogenous fertilizers, and of Krupp-Treibstoffwerk were given priority. Nothing further has been heard about another conversion project for the use of Fischer-Tropsch plants exempted from dismantling for paraffin synthesis.

499. ———. Sensitive Pressure Controller in Hydrocarbon Synthesis. Vol. 63, 1950, pp. 59-60.

Very efficient sensitive pressure controller is described. The basic principle of the device is the well-known use of a ball valve held on its seating by a tension spring. It is at present operating on a fluid bed, Fischer-Tropsch process, and maintains a constant 20 atm. pressure at gas-flow rates of 2 to 60 cu. ft. per hr. It is capable of maintaining a preselected pressure for indefinite periods without supervision. The control limits can be broadened by changing the tension of the spring.

500. ———. Fluid-Bed and Liquid-Phase Slurry Process. Vol. 64, 1951, pp. 773-775.

Compares 2 processes. The British Fuel Research Station is making an investigation for the purpose of improving the conventional Fischer-Tropsch process. A large-scale pilot plant is being erected.

500a. ———. Fuel Research Since the War. Vol. 65, 1951, pp. 721-726.

Fuel Research Board of Great Britain reports on a study made during the 3 yr. ending March 31, 1949, on the enrichment of water gas by the conversion of the CO and H<sub>2</sub> to CH<sub>4</sub>. A reactor to treat 100-200 ft.<sup>3</sup> of water gas was constructed, in which the granular catalyst was placed in a vertical perforated tube 6 ft. by 1.25 in. enclosed in a water-jacketed steel tube 1.50-in. inside diameter. The water gas entered this tube at the bottom, flowed up the annular space, and reached the catalyst by free diffusion, the products of the reaction then diffusing back into the main gas stream. This arrangement permitted of obtaining a uniform temperature distribution along the length of the tube without deposition of C and a preferential consumption of H<sub>2</sub> so that gases of low H<sub>2</sub>:CO ratio, such as blue water gas, could be used without addition of H<sub>2</sub>. From time to time as the catalyst deteriorated, a part of the charge was discharged at the bottom and a fresh amount added at the top by gravity feed. With the circulating H<sub>2</sub>O at 200°, the catalyst temperature was at 350°-375°. Using a Ni-kieselguhr 1:1 catalyst, the plant performance, when producing enriched gas of 456 B. t. u. per ft.<sup>3</sup> was equivalent to a yield of 2,100 lb. of CH<sub>4</sub> per lb. of Ni in the catalyst, which had a useful life of 168 days. Kieselguhr was found to be an essential promoting constituent of the catalyst. Reduced NiCO<sub>3</sub> preparations made without the addition of kieselguhr showed no activity for CH<sub>4</sub> synthesis <300°, whereas reduced NiCO<sub>3</sub>-kieselguhr catalysts were active at temperature as low as 150°. Synthesis with a fluidized bed of sintered Fe catalyst was investigated at 300°-340° at 20 atm. pressure with the synthesis-gas rate 750-2,050 vol. per vol. catalyst per hr. and with recirculation of residual gas at a velocity of 0.4-0.7 ft. per sec. to maintain the bed in a fluidized state. Yields of hydrocarbons higher than CH<sub>4</sub> per unit vol. of catalyst per hr. were obtained up to 30 times those obtainable by the conventional synthesis with Co catalyst. Difficulty was experienced with expansion and disintegration of the catalyst granules by deposition of nonvolatile products in the pores. Suspension of a powdered Co catalyst in molten wax (synthesis product) by recirculation of residual gas at the proper velocity was also tried. To obtain results equal to those with the conventional fixed bed of catalyst, temperatures 10°-15° higher were required. Maintenance of space velocities higher than 200 per hr. caused a rapid reduction in catalyst activity. The products obtained by liquid-phase synthesis were

found to be more volatile than those obtained by normal operation at the same temperatures. In studying the Co catalyst, it was found that a freshly reduced one did not give the X-ray diffraction pattern of Co. That the catalyst does not contain bulk metallic Co is confirmed by measurement of the surface areas of the catalysts and their components. It is considered that the reaction takes place on isolated Co atoms and not on bulk metallic Co or by way of bulk Co carbide. It is suggested that under certain conditions CH<sub>4</sub> present in the synthesis gas can take part in the reaction. Also, wax formed on the catalyst during synthesis reacts with H<sub>2</sub> to yield higher hydrocarbons distributed among the different molecular sizes in a way similar to the distribution of the synthesis products. These 2 facts, taken together, suggest that the final stages of synthesis involve a polymerization-depolymerization equilibrium. When synthesis is carried out at abnormally low temperatures and low times of contact, appreciable quantities of alcohols are present in the products produced by Co catalysts. These results, together with observations on the decomposition of alcohols under synthesis conditions are consistent with the view that the alcohols are the true primary products of the synthesis reaction.

501. ———. Sulfur Recovery in Germany. Vol. 64, 1951, pp. 373-376.

Review of various methods adopted in Germany to combat the shortage of S is given. They are divided into (a) dry-recovery processes; (b) wet-recovery processes, such as the Thylox, Dutch Mines, and Katalusul processes; and (c) scrubbing with an organic liquid, such as the Alkaid and the Girbotol processes. References are made to technical documents on British FD microfilms.

501a. ———. Expanding Horizons for Oxo Petrochemicals. Vol. 67, 1952, pp. 95-96.

Importance is stressed of the Oxo process to the petroleum refiner in upgrading byproduct olefins to aldehydes, alcohols and other petrochemicals.

502. CHEMICAL AND ENGINEERING NEWS. Catalysts Investigated for Synthesis of Methane. Vol. 22, 1944, pp. 19, 1710.

Work on the synthesis of CH<sub>4</sub> has been carried on both at the Gas Research Board (British) and at the Fuel Research Station (British). A preliminary exploration has indicated that a Ni catalyst is likely to give a satisfactory rate of conversion at a high space velocity. At the Fuel Research Station most of the work has been carried out using water gas. With water gas of a high H<sub>2</sub>:CO ratio, the most suitable catalyst for work at a relatively low temperature has proved to be a Ni catalyst promoted by ThO<sub>2</sub> and supported by kieselguhr. For the removal of S from water-gas mixture, a Cu-Cr catalyst supported on active C was developed at as low a temperature as 250° C. A hydrogenating catalyst of the MoS<sub>2</sub> type is required to protect the poisoning of the Cu-Cr catalyst when coal gas is used. A method for complete decomposition of thiophen was developed with a MoS<sub>2</sub> catalyst at 300° C.

503. ———. Fischer Summarizes Wartime Progress in Synthetic Oil Research. Vol. 22, 1944, p. 391.

Digest of a review of the various processes using C oxides and H<sub>2</sub> for the production of synthetic oils. Normal-pressure synthesis, medium-pressure synthesis, and the use of Ni, Co, Ru, and Fe catalysts are briefly touched upon.

504. ———. Ketones From Fischer-Tropsch Process. Vol. 22, 1944, p. 2114. Petrol. Times, vol. 48, No. 1234, 1944, p. 747.

Extensive experiments have been carried out in Germany with fatty acids from the Fischer-Tropsch

process with a view to the production of ketones. The fatty acids were saponified with lime and the resulting calcium salt subjected to dry distillation. A mixture of ketones of great variety was obtained. Experiments were carried out with fractionated fatty acids, and these showed that the ketones obtained corresponded closely in boiling and solidification range to the theoretical figures. Various types of ketones were obtained. Some were liquids with a pleasant odor, others were white solids of waxlike appearance. They can be used in the cosmetics industry or as plasticizers.

505. ———. Lignite-Gasification Plant at Grand Forks, N. Dak. Vol. 23, 1945, pp. 1242-1244.

Federal Bureau of Mines commercial-size pilot plant for the gasification of lignite is described, and a flow sheet of the operation is shown. The process as used is a combination of the Reyerson low-temperature, continuous, isothermal system with the Farry vertical, annular, externally heated retort but over a wider range of temperature. Part of the water gas produced is formed by the reaction between the fresh lignite and its contained moisture in the upper zone, while the balance comes from the lower zone in which the lignite char reacts with steam passed countercurrently from the bottom of the retort. The 2 streams of water gas combine and pass out at the top through the center. The system is designed for an output of 75-80 cu. ft. of water gas per hr. per sq. ft. of heated retort surface. The unit produces 33,000 cu. ft. of a 300-B. t. u. gas per ton of lignite containing 70-72% of H<sub>2</sub>. The H<sub>2</sub>:CO ratio can be varied from 1.8 to 12, with changes in temperature and concentration of steam. The highest ratios giving maximum H<sub>2</sub> production are obtained at low temperatures, while at higher temperatures a synthesis gas, which is high in CO and suitable for use in Fischer-Tropsch reactions is obtained.

506. ———. New Sources of Fats Sought in Germany. Vol. 23, 1945, p. 1884.

The rapidly developing synthesis of hydrocarbons with fatty acids in the last 10 yr. (directly from CO<sub>2</sub> and H<sub>2</sub>, or from hydrocarbons) suggested that the synthesis of fats (through esterifying fatty acids with glycerol) could soon be attempted on a large scale. In practice, however, it became apparent that the road from the fatty acid to an edible fat is extremely complicated and expensive. This is the reason why direct synthesis has not been taken up on a large technical scale. Synthetic fat is used in U-boats, however, because it never gets rancid. Actually Imhausen synthesis furnished a high-quality edible fat. Because of the above-mentioned unsatisfactory aspects of a total fat synthesis from CO<sub>2</sub> and H<sub>2</sub> by ester formation, recourse was made to biochemical methods. In this field fundamental progress was made. Some researchers succeeded in growing fat-producing fungi (yeasts, fusaria), on entirely synthetic mediums. The source of C for this synthesis is sugar (also pentose). With this method it is easy to obtain fats from timber by way of sugar. After approximately 48 hr. these fungi contain 15% of the original sugar supply in form of fat, which is suitable for human consumption. In addition, approximately 15% protein is formed. The necessary N<sub>2</sub> is derived from ammonium salts, nitrates, urea, amides, or easily synthesized amino acids.

507. ———. Oxo-Process Chemicals. Vol. 27, No. 4, 1949, p. 245.

Rohm & Haas Co. has announced the availability of 6 new chemicals derived from the Oxo process. A pilot plant has been constructed for preparing aldehydes catalytically from olefins, CO and H<sub>2</sub>. The olefin first chosen for the process is diisobutylene, which reacts by the Oxo process to give only 1 isomer. The carbonyl group becomes attached to the terminal C to



produce 3,5,5-trimethylhexaldehyde. The 6 chemicals now available are derived from this nonyl aldehyde: Nonanoic acid, nonylamine, nonyl aldehyde cyanohydrin,  $\alpha$ -hydroxydecanoic acid, octadecenyl aldehyde, and octadecyl alcohol. Some potential uses for these products are enumerated.

508. ———. Blaw-Knox Fuel Synthesis. Vol. 28, No. 5, 1950, p. 331.

Blaw-Knox Co. has announced the formation of a chemicals- and fuels-synthesis department. The new activity will deal with the conversion of fuels into chemicals and will be based initially on the Fischer-Tropsch synthetic fuels process and on related processes for making synthesis gas. An agreement has been made with Ruhrchemie and Lurgi for licenses and access to all process information developed by these German firms. The new department will adapt processes, develop pilot plants, design equipment, provide engineering, and built plants for converting plentiful fuels into more valuable chemical materials and upgraded forms of hydrocarbons.

509. ———. Cost of Synthetic Fuels. Vol. 28, No. 15, 1950, pp. 1187-1189.

Analytical summary of the economic features of the annual report of the Secretary of the Interior on the synthetic liquid fuels program.

510. ———. Synthetic Fuels Plant for India. Vol. 29, 1951, p. 1136.

Announcement has been made of plans for construction of a plant for the Kalaga Synthetic Oil Corp., Ltd., of Cuttack, Orissa, by Cie. Pan-Européenne d'Installations et d'Équipement Industriels de Paris and Ruhrchemie A.-G. of Germany. The plant will have an initial capacity of 10,000 tons, expandable later to 100,000 tons. Synthesis gas will be made from powdered coal by total gasification. The Indian Government has agreed to buy the entire output of gasoline. 5 Indian students, who have been studying in Paris for 2 yrs., will operate the plant. Production is expected to begin in 1952.

511. CHEMICAL AND METALLURGICAL ENGINEERING. Germans Investigate Methods for Processing Lignite. Vol. 41, 1934, p. 666.

Among competing projects must be mentioned the method by Prof. Franz Fischer, the leader of the Kaiser Wilhelm Institute for Coal Research in Mülheim. Petroleum products, from gasoline to high-melting paraffins, may be produced synthetically from water gas, mixtures of CO and H<sub>2</sub>. The process has been developed to the point where 160 gm. gasoline is obtained per m.<sup>3</sup> gas at atmospheric pressure and a temperature below 200° C. with aid of highly active catalysts (alloy skeletons, see abs. 512). By an oil-circulation system the temperature of the catalyst may be kept at the optimum. The first industrial pilot plant will be started in the near future by Ruhrchemie A.-G. Coal, coke, lignite, peat coke, and charcoal may all be used as raw materials. With a coke price of RM. 18 gasoline may be produced at a cost of RM. 0.22 per kg. or RM. 0.105 per l. It is hoped that an increased yield may permit a reduction in this cost.

512. ———. Synthesis of Liquid Hydrocarbons. Vol. 41, 1934, p. 215.

It is possible with highly active Co or Ni catalysts, which reach maximum capacity at 200° C., to treat a gas CO : H<sub>2</sub> :: 1 : 2 with almost complete conversion of CO in 1 pass, with up to 70% liquid hydrocarbons. Fischer has lately succeeded in replacing the precipitation catalyst formerly used with skeletons of alloys, which take up only 1/6 of the volume occupied by the precipitated catalysts with almost the same capacity. Ni-Al alloy, as well as Ni-Si, Co-Si, and Ni-Co-Si were used, from which the Al and Si were dissolved by

caustic potash leaving a skeleton of the heavier metals, Ni : Co : Si :: 1 : 1 : 2 proved most effective. Almost 100 cm.<sup>3</sup> liquid hydrocarbons was produced from 1 m.<sup>3</sup> of gas mixture in 1 pass.

513. CHEMICAL ENGINEERING. Oxygen, Past, Present, and Prospects. Vol. 54, No. 1, 1947, pp. 123-131.

The search for cheap O<sub>2</sub> (that containing from 88-98% O<sub>2</sub>) has received considerable impetus recently, and it appears likely that such a low-purity O<sub>2</sub> can be produced for a small fraction (about 4% or less) of the present cost of high-purity gas, provided it is made in large units, operated at substantially constant rate, and installed at the point of use. Estimates of costs range from \$0.048 for 1,000 cu. ft. of 95% O<sub>2</sub> in a plant of 48,000,000 cu. ft. per day capacity to an average of \$0.12 including all the factors in power cost. In Germany the Linde-Fränk, low-cost low-purity O<sub>2</sub> process was able to produce 98% O<sub>2</sub> in a large plant for 1.53 pf. per m.<sup>3</sup> (\$0.10 per 1,000 cu. ft.). Of the total costs, power cost amounted to 58.8%, depreciation 31.4%, wages 4.9%, and water, lubricating oil, and chemicals 4.9%. Much research has been done in the United States and developments by several companies are commented upon, and a number of applications for cheap O<sub>2</sub> are presented. The principal uses include hydrocarbon-synthesis, steel-industry, and gas-industry applications, the technical feasibility and the economic justification of which still require further proof.

514. ———. Recent Developments in Fuel Technology. Vol. 54, No. 4, 1947, pp. 127-132.

Review, particularly of the progress in Fischer-Tropsch practice in the United States.

515. ———. Liquid Fuels From Lignite in Australia. Vol. 53, No. 9, 1948, p. 236.

After several months of research and study by German scientists, one of them familiar with the development of the Lurgi process for gasification and liquefaction of coal, it has been decided that the brown coal of Victoria is suitable for gasification and as raw material for synthetic-gasoline plants. The expectation is that American pilot plants will be purchased and installed.

516. ———. South Africa Plant to Get Oil From Coal. Vol. 55, No. 1, 1948, pp. 207-208.

The Anglo-Transvaal Consolidated Investment Co. will erect an oil-from-coal plant at Vereeniging, South Africa. According to A. S. Herscov, chairman, the plant will be a replica of the Standard Oil of Indiana plant at Hugoton, with incorporation of improvements in the plant at Brownsville. Hydrocarbon Research, Inc., will act as technical consultant. The plant will cost about £14,000,000.

517. ———. Synthetic Fuels. Vol. 55, No. 6, 1948, pp. 131-138.

Review of developments and the future possibilities in synthetic liquid fuels production.

518. ———. Synthetic Fuels Program for India. Vol. 55, No. 9, 1948, p. 225.

Study is being made by the Koppers Co. looking toward establishment of a state-owned synthetic-petroleum industry based on gasification of low-grade coal. Costs are being calculated for plants of various capacity from 100,000 tons to 1,000,000 tons annually of gasoline and byproducts. Preliminary estimates for a 1,000,000-ton plant place the cost at \$150,000,000 plus the outlay for a 200,000-kw. power plant.

519. ———. New Way to Make Heavy Water. Vol. 57, No. 3, 1950, p. 69.

Atomic Energy Commission plans construction of a plant to produce heavy water by a new and much cheaper process at only about one-fifth of the old cost. The process to be employed is low-temperature distil-

lation of extremely large volumes of H<sub>2</sub>, such as are obtained in the off gas from large synthetic fuels or synthetic NH<sub>3</sub> plants. Total estimated cost of a plant at existing synthetic plants is \$5,000,000. Surveys are under way to determine the selection of a plant site. There are about 20 synthetic NH<sub>3</sub> plants in the United States.

520. ———. Methanol Today. Vol. 58, No. 6, 1951, pp. 285-287.

Two major processes are being used to produce synthetic MeOH: Reaction of CO and H<sub>2</sub> and oxidation of selected fractions of natural or C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>. Synthetic MeOH producers are listed. Estimated production costs are \$0.138 per gal., net profit about \$0.095 per gal. The major % uses of MeOH are shown. Synthetic production in 1951 should be about 160 million gal. and will probably reach 200 million gal. by 1953.

520a. ———. Fischer-Tropsch Makes Progress. Vol. 58, No. 2, 1952, p. 250.

Progress made in the operation of the improved Bureau of Mines reactor at Louisiana, Missouri. The new reactor converts 73-85% of the synthesis gas to oil. If conversion can be raised to 90%, the process can be operated in 1 stage instead of 2. Overall costs are being reduced.

521. CHEMICAL INDUSTRIES. Alcohols Above C<sub>2</sub> Produced From Olefins, Carbon Monoxide, and Hydrogen. Vol. 60, 1947, pp. 232-233.

Description of the Oxo process for the synthesis of primary alcohols by the interaction of olefins, CO, and H<sub>2</sub> over a Fischer-Tropsch catalyst. Information is taken from Bureau of Mines Information Circular 7370.

522. ———. New CO-H<sub>2</sub> Converter Provides Better Temperature Control. Vol. 60, 1947, p. 793.

Close control of the reaction temperature in the newest Bureau of Mines Fischer-Tropsch converter is achieved internally by vaporizing a hydrocarbon oil from the catalyst surface, instead of by means of heat exchangers alone, as in German practice, or by a fluidized fixed catalyst bed with a heat exchanger, as is proposed in the commercial installations under construction in the United States. In operation, a fraction of the liquid reaction product (boiling 110°-125°) is passed in parallel flow, along with the synthesis gas, through the column of pelleted Co catalyst at 100-150 p. s. i. and at a space velocity of about 1,000 lb. per m.<sup>3</sup> of catalyst per day. As heat is liberated by the reaction, vaporization of the injected liquid holds the temperature of the catalyst at the desired point, about 200°. In one continuous run of over 600 hr., no appreciable loss in catalyst activity was experienced. The method has another advantage in the removal of the high-melting waxes that have always blinded the surface of the Co catalysts after a short period of operation. It is estimated that an internally cooled unit should cost about the same as the fluid catalyst unit per bbl. of hydrocarbon product per day. Furthermore, it provides a more flexible operation.

523. ———. Production of Fatty Acids by Air Oxidation of Paraffin Wax. Vol. 60, No. 1, 1947, p. 64.

Reviews German method as practiced at Oppau. (See Bureau of Mines Information Circular 7376, abs. 1494 and 1495). The paraffin wax used may be produced by the hydrogenation of brown coal, from petroleum or from the Fischer-Tropsch synthesis. In any case, it should consist of straight-chain hydrocarbons, with only small amounts of branched-chain or cyclic hydrocarbons. The preferred chain length is C<sub>12</sub>-C<sub>20</sub> and S compounds, and phenols should not be present as they inhibit the oxidation.

524. ———. Separation by Adsorption. Vol. 61, 1947, pp. 625-631; Fuel Abs., No. 3506, June 1948.

Summary of the development of adsorption as a method of separation is given with reference to the production of activated C from bituminous coal, methods for the activation of C, and hydrocarbon fractionation by means of fixed beds of C attached to Fischer-Tropsch converters and operated in a manner similar to the chromatographic separation of various components of solutions and by the hypersorption process. The adsorbent C falls through a tower countercurrently to hydrocarbon vapors. As the C falls, it adsorbs the lighter constituents. Lower down the C meets with a greater concentration of heavier constituents, which displace the lighter material. Thus, throughout the length of the column, an effect is produced comparable to refluxing in distillation. The bottom section consists of a steaming section in which adsorbed material is stripped from the C. In a C<sub>2</sub>H<sub>4</sub> recovery unit now in operation, 76,900 cu. ft. of gases containing 5.7% of C<sub>2</sub>H<sub>4</sub> are fed into the tower per hr., and approximately 7,000 lb. of a product containing 92% of C<sub>2</sub>H<sub>4</sub> is obtained per day. Activated C has been employed to recover antibiotics.

525. ———. Oxoated Olefins. Vol. 63, No. 2, 1948, pp. 211-212.

First commercial application of the Oxo synthesis is now under way by the Esso Standard Oil Co. at Baton Rouge in the high-pressure petroleum hydrogenation unit. Iso-octyl alcohol is being produced. The price is expected to be somewhat under \$0.30 per lb. It is to be used in making plasticizers. Other organizations are making plans also: Standard Oil Co. of Indiana will produce nonyl alcohol at its Whiting plant; the Oronite Chemical Co., Texas Co., and duPont are also interested in the production of high-molecular-weight alcohols, as is the Shell group in its petrochemical plant in England.

526. ———. Fischer-Tropsch Fats. Vol. 64, No. 6, 1949, pp. 914-915.

Food and Agriculture Organization of the United Nations has made a study of synthetic fats and presents the conclusion that more information on all phases of the problem is necessary before large-scale fat synthesis is advocated. It is not yet clear whether synthetic fats are suitable as human food. The production of artificial fats for industrial use in the making of soaps, detergents, greases, etc., is practical and would release a like amount of natural fats for food in countries such as Germany, where fats are in short supply. German capacity for synthetic fats production is 11,700 tons/yr. at present.

527. ———. From Wood Distillation to Oxo. Vol. 66, No. 6, 1950, p. 826.

Tennessee Eastman Corp. has been producing a small amount of isobutyraldehyde as a byproduct from its Oxo pilot plant. A petrochemical plant is being constructed at Longview, Tex. The major product is to be n-butyric acid for the production of Tenite II, a cellulose acetate-butyrates plastic. The process to be used is a modification of the Oxo-synthesis. Propylene (presumably produced by propane cracking) will be reacted with a mixture of CO and H<sub>2</sub> to form a mixture of n-butyraldehyde and isobutyraldehyde. These will be fractionated, and oxidation of the latter compound will give n-butyric acid.

527a. CHEMICAL TRADE JOURNAL. Synthetic Fuels in South Africa. Vol. 129, 1951, p. 337.

Some of the technical features of the Coalbrook project are presented. Production of about 200,000 tons of liquid fuels annually will be based on a combination of improved German and American versions of the Fischer-Tropsch process, the former being a develop-

ment of the Ruhrchemie and Lurgi companies, the latter of M. W. Kellogg Co. The principal difference between the 2 methods lies in the actual synthesis stage, especially in the types of reactor vessels, catalysts, and process techniques. The coal with 26-29% ash content will be gasified in a Lurgi pressure plant thus enabling the gas to be generated under the actual pressure used for the subsequent synthesis, 300-450 p. s. i. The Ruhrchemie-Lurgi's "Rectisol" process will be used for the gas purification. The combined process is considered the most advantageous economically because of the greater flexibility of operations. Whereas Kellogg's powdered-catalyst method yields essentially fuels, the Ruhrchemie-Lurgi process may be directed either to fuels production or to a larger output of paraffin wax and base stocks for chemical manufacture. Improvements in the fixed-bed technique of the German process permits an increase in the daily output capacity from an average of 2 to about 50 tons/day. It is expected that 50,000 tons/year of primary products will be obtained from the Ruhrchemie-Lurgi plant, and 150,000 tons from the Kellogg plant, which will use the tail gas from the German plant in the synthesis operation.

528. CHEMICAL TRADE JOURNAL AND CHEMICAL ENGINEER. Hydrocarbon Synthesis From Water. Vol. 99, 1936, p. 50.

Wintershall A.-G. of Berlin and Kassel is to manufacture synthetic fuel by a modification of the Fischer-Tropsch process and for this purpose has founded a subsidiary styled the "Mittel Deutsche Treibstoff und Oelwerke A.-G.", with headquarters in Kassel and an initial capital of RM 500,000. The new plant, which is being financed entirely by the Wintershall Co., is expected to start in the middle of 1937. The process employed has been established on the experimental scale at a plant at the Raunel Nitrogen Works, which the Wintershall Co. erected in cooperation with the Klockner Co.

529. ———. Fischer-Tropsch Process in France. Vol. 100, 1937, p. 212; Gas Times, vol. 13, No. 153, 1937, p. 38.

A plant for the production of motor spirit from coke has recently been put into operation at Harnes in the Pas de Calais district of France. This plant, which is based on the Fischer process, has been designed for an annual production of 20,000 tons of spirit.

530. ———. New Fischer-Tropsch Plant. Vol. 101, 1937, p. 346.

A new company, the Kator-Fabrik Lutzkendorf G. m. b. H., has been formed in Mfichen, Geisenthal, with a capital of 1.5 million RM for the sole purpose of manufacturing catalyst for use in the Fischer-Tropsch process.

531. ———. Production of Motor Fuel in Germany. Vol. 101, 1937, p. 592.

Total capacity of all Fischer-Tropsch plants in operation or under construction in Germany is 700,000 tons per yr. as against 1,900,000 tons by the hydrogenation process. It will be several years before these ultimate capacities can be attained, the anticipated production for 1938 being 250,000 tons and 900,000 tons, respectively.

532. ———. Synthetic Fats. Vol. 105, 1939, pp. 235-236.

It is reported that Germany is to embark on large-scale production of synthetic edible fats made from glycerin and the acids obtained from Fischer-Tropsch wax. It is assumed that the glycerin would be synthesized from propylene. The synthetic product would differ from the natural fats primarily in that the component synthetic acids have both odd and even numbers

of C atoms. These synthetic fats appear to be assimilated without any physiological disturbance to the human system.

533. ———. Edible Fats From Fischer-Tropsch Wax. Vol. 105, 1940, p. 235.

References to large-scale experiments on the production of "ersatz" fats by the interaction of glycerin with the fatty acids made by the catalytic oxidation of the paraffin wax from the Fischer-Tropsch process have been frequent in the continental press over the past year or so. Production of glycerin by fermentation of sugar solutions, a process used by Germany in 1914-18, may be revived, but it is more likely that the all-synthetic route to glycerin from propylene will be the one chosen.

534. ———. Iron Catalyst. Vol. 108, March 1, 1941, p. 8.

New Fe catalyst that has been developed recently in the laboratory of Dr. Kita of the Kyoto Imperial University is claimed to be quite as efficient as the German Co catalyst in the production of synthetic petrol by the Fischer-Tropsch and allied processes. A pilot plant for its utilization is to be erected. (See British Patent 529,390, abs. 1861.)

535. ———. Fatty Acids From Paraffins. German Experience With Wartime Process. Vol. 116, 1945, pp. 300-311; Die Chemie, vol. 57, No. 1-2, 1944, pp. 6-11.

Review of the article by L. Mannes (abs. 2170). In the development of a fatty acid industry in Germany for the manufacture of soap and the production of substitutes for the natural edible fats, it was found that the principal suitable material available in Germany was the waxy, paraffinic byproduct produced in the synthesis of gasoline by the Fischer-Tropsch process. This product at ordinary temperatures is virtually wholly hydrocarbons, partly liquid and partly solid, with iso- and branched-chain compounds, these latter increasing rapidly as the number of C atoms in the Fischer-Tropsch byproduct increases. In practice it was found that, even with the closest control of the oxidation and refining stages and the use of the choicest hydrocarbon raw material, numerous undesirable and overoxidized byproducts were produced, which lowered the yield and detracted from the qualities of the fatty acids of 10-20 C atom range. By the introduction of improved catalysts, accurate temperature control, and the avoidance of overoxidation there has been some improvement in the quality of the desired product. Figures quoted from laboratory investigations on the catalyst oxidation of Fischer-Tropsch paraffin wax residues show that out of a total fatty-acid yield of 55-60%, 20-25% consists of fatty acids with C atoms ranging from 1-9, and of this latter amount 1/2 consists of fatty acids ranging from formic to butyric. Further, about 10% of the paraffin is oxidized to CO<sub>2</sub> with a little CO. From the results reported it would not appear that the production of fatty acids by paraffin oxidation is a process that holds much inducement to any country having reasonable supplies of natural fatty acids.

536. ———. South African Synthetic Fuel Plans. Vol. 121, 1947, p. 484.

Anglo-Transvaal Consolidated Investment has plans to erect a new oil-from-coal plant on Vaal River near Vereeniging. Hydrocol Corp. will act as consultants. The plant will have a capacity of 60,000,000 gal. of high-octane gasoline and 9,000,000 gal. of Diesel oil yearly. South Africa will start with low-grade coal to make synthesis gas, but the subsequent processes are identical with the American modification of the Fischer-Tropsch process.

537. ———. Coal Oils in South Africa. Vol. 123, 1948, p. 503.

Union Government has published a copy of the draft license it proposes to grant to Anglo-Vaal Consolidated

Investment Co. for producing liquid fuels from coal. The following stipulations are given: Production shall be started within a period of 4 years. Production is to be 70,000-100,000 gal. per yr. The process to be used is the generation of gases from C material and the catalytic conversion of the gases to petrol and petroleum-like hydrocarbons. The coal used shall be from the deposits in Vrededorf in the Orange Free State. All of the coal in each seam is to be used, and no coal containing less than 30% ash is to be rejected, unless it can be proved that the properties of such coal, other than its ash content, render it unsuitable for this purpose. The Government will not grant a similar license to any other concern for a period of 4 yr.

538. ———. South African Synthetic Petrol Plans. Vol. 122, 1948, p. 44.

In his statement for the general meeting of Anglo-Transvaal Consolidated Investment Co., Ltd., at Johannesburg, Dec. 19, 1947, A. S. Herscov reported that rights to the synthetic petrol process developed by Hydrocarbon Research, Inc., had been obtained. Application has been made for license to produce 60,000,000 gal. of petrol and 10,000,000 gal. diesel oil per yr. The factory will cost £12,000,000-£12,500,000 and take 2-3 yr to erect.

539. ———. Synthetic Fatty Acids. Vol. 122, 1948, p. 70.

Production of synthetic fatty acids, on a limited scale, has been resumed by Deutsche Fettsäurewerke at Witten since small amounts of Fischer-Tropsch Gatsch have been received with the restarting of the Fischer-Tropsch plants at Castrop-Rauxel and Wanne-Eickel. These Witten works were idle from the end of the war until September 1947.

540. ———. German Fischer-Tropsch Plants. Vol. 125, 1949, p. 410.

According to information in the German press, the Fischer-Tropsch plants that were operating in Bizonia during the first half of 1949 produced 28,140 tons primary products compared with 24,838 tons, January-June 1948. The yield in finished products was: Benzene, 10,519 tons; kogasin I, 2,453 tons, kogasin II, 4,453 tons, paraffin Gatsch, 2,949 tons; and hard paraffin, 970 tons.

541. ———. Germany's Synthetic Oil Plants. Vol. 124, 1949, p. 336.

Production of synthetic petrol and oil in Germany is still prohibited. At present 2 plants using the Fischer-Tropsch process are producing primary materials for the manufacture of fatty acids and synthetic detergents for the soap and washing-powder industry. Permission has been given for 2 plants, originally built for hydrogenation of coal by the Bergius process, to be used to a limited extent for the hydrogenation of residues from the initial refining of imported crude oils and also for the production of synthetic ammonia.

542. ———. Hydrocol's New Hydrocarbon Synthesis Plant Approaching Completion. Vol. 124, 1949, p. 689.

Initial production is expected before the end of the year. Coproducts of the new plant, in excess of 300,000 lb. of water-soluble oxygenated compounds, are to be separated and refined by Stanolind Oil & Gas Co. to yield methyl, ethyl, n-propyl, n-butyl, and n-amyl alcohols; acetaldehyde, propionaldehyde, and butyraldehyde; acetone, methyl-ethyl ketone, methyl-propyl ketone, and methyl-butyl ketone; and acetic, propionic, and butyric acids. These products will be distributed by United States Industrial Chemicals, Inc.

543. ———. Leuna Works Production. Vol. 125, 1949, p. 410.

Leuna Works near Merseburg (Russian zone) produced 150,000 metric tons of nitrogenous fertilizers in

1948-49, according to "Aufbau". The plant is again producing Buna synthetic rubber. Oil hydrogenation is 25% of prewar rate.

544. ———. Synthetic Fatty Acids in Germany. Vol. 125, 1949, p. 410.

According to Die chemische Industrie, Düsseldorf, the Hydrierwerk of Rodleben near Rosslau (formerly Deutsche Hydrierwerke) is building a plant for production of fatty acids by oxidation of paraffin. The material is to be used in the manufacture of soap. The new plant will have an annual capacity of 6,400 tons per year. The first section, 185 tons per mo., is expected to be ready soon.

545. ———. Fischer-Tropsch Plants. Vol. 126, 1950, p. 616.

Both the Government and private pressure groups in western Germany are doing their utmost to keep some of the Fischer-Tropsch plants intact and in operation. As the manufacture of synthetic-oil products is now a prohibited industry and as the need for running the plants for the production of Gatsch is no longer urgent, the Federal Ministry of Economics has submitted to the Allied experts a memorandum suggesting conversion of the remaining plants to the synthesis of alcohols. The Germans now maintain that, by suitable modification, the process can be operated without production of any hydrocarbon fractions. The conversion can be completed in 6-8 months. The views of the Allies are not known. In another direction the Federal German Government has already been successful in negotiations with the Allies. They have agreed that Gelsenberg-Benzin A.-G. will resume refining this month, though not by the Bergius high-pressure hydrogenation process. The main charging stock will be crude oil from the Emsland fields, of which large supplies exist, supplemented by imported oil from the German-American Oil Co., Ltd. The monthly output is expected to be 15,000-20,000 tons petrol, 5,000-10,000 tons diesel oil and about 1,000 tons gas oil.

546. ———. Germany's Oil Industry—Fischer-Tropsch Plants Not To Be Restarted. Vol. 126, 1950, p. 984.

Regarding rumors that Fischer-Tropsch plants in the Ruhr were still producing despite the Allied ban, a high official of the American High Commission's fuel and power branch reported that the last 2 plants working on the method had closed down Dec. 31, 1949, when a temporary allied production permit expired. The North Rhine-Westphalian Economics Ministry has shown a cold shoulder to German industrialists' hopes for reviving the industry. While prices of basic materials, especially coke, had risen by up to 150%, sales prices for products had risen no more than 50%. The price of catalysts was 3 times the prewar level, since the only West German plant producing the catalysts, at Oberhausen-Holten, was working at considerably reduced capacity. Gelsenberg Benzin A.-G. at Gelsenkirchen and Union Rheinische Braunkohlen-Kraftstoff A.-G. at Wesseling are making petroleum from crude oil by the high-pressure Bergius hydrogenation process from German and imported crude oil. Together they are expected to process 1,000,000 tons of crude oil this year and 2,000,000 tons by 1952. No new plants operating on the Bergius process will be built in West Germany. More cracking plants are planned.

547. ———. Indian Coal-Oil Plans. Vol. 126, 1950, p. 1435.

Indian Government has granted a license to B. Patnaik as sponsor for erection of a Fischer-Tropsch plant at Talcher in Orissa on the eastern seaboard. Production is expected to begin some time in 1951. The

plant, coming from the French zone of Germany, will have an output of 10,000 metric tons/yr. The Government has also contracted with Koppers Co. United States, to prepare plant designs for utilizing lower-grade Indian coals for synthetic-oil manufacture by hydrogenation. The plant will have an output of 100,000 metric tons of products/yr. and will require a capital investment of 220,000,000 rupees (\$16.5 million).

548. ———. German Oil Processing. Vol. 128, 1951, p. 36.

Ruhrchemie A.-G. and the Omnipetrol Oil Processing Co. of Karlsruhe (representing the West German interests of the Omnium Français Pétroles) have concluded a contract providing for close cooperation in oil processing. The contract provides for the repair of Fischer-Tropsch installations of the Ruhrchemie A.-G. and the construction of a refinery at Oberhausen. The crude oil supplied by Omnipetrol from the Middle East will be finished by Ruhrchemie A.-G. A processing capacity of 200,000 tons is planned. The oil will be topped in a distillation plant and the residues processed in a cracking plant. Diesel oil, heating oil, and refinery gas will be produced in addition to gasoline. Gasoline output is estimated at 100,000 tons/yr. The cost is estimated at about 10,000,000 RM.

548a. CHEMIKEN-ZEITUNG. [Synthetic Fuels Production.] June 15, 1951; Chem. Trade Jour., vol. 128, 1951, p. 1502.

Chemische Werke Bergkamen, the Krupp Treibstoff A.-G. of Wanne-Eickel and the Gewerkschaft Viktor of Castrop-Rauxel, have decided that the present price of coal renders resumption of liquid fuels production by the Fischer-Tropsch process uneconomical. The 3 companies are to operate their plants only for the production of hard paraffins, propyl alcohol and materials which can be processed into synthetic detergents.

549. CHEREPENNIKOV, A. A. [Chemical Application for Methane From Natural Gas.] Neftyanoe Khoz., vol. 18, 1930, pp. 796-799; Chem. Abs., vol. 25, 1931, p. 397.

Review of the literature comprising chlorination, oxidation, water-gas reaction, reaction with CO and CO<sub>2</sub>, decomposition into C and H<sub>2</sub>, and preparation of higher hydrocarbons, carbides, and HCN.

CHERKOV, I. B. See abs. 151.

CHESEBRO, P. R. See abs. 2600.

CHESSICK, J. J. See abs. 1372.

550. CHEVALIER, R., AND BÉGUI, Z. E. [Thermomagnetic Properties of Ferric Oxide.] Bull. soc. chim., vol. 4, No. 5, 1937, pp. 1735-1742; Chem. Abs., vol. 32, 1938, p. 3219.

Coefficients of magnetization,  $\chi$  at 20° and 720°, were measured by Curie's method, for some 20 Fe<sub>2</sub>O<sub>3</sub> samples differing in preparation. For these the Curie point is remarkably constant between 690° and 700°. Above this temperature,  $\chi$  is constant, with a mean value of  $19 \times 10^{-6}$  at 720°, even when the oxides contain traces of impurities. This value appears to be a lower limit for the susceptibility of Fe<sub>2</sub>O<sub>3</sub>, and characterizes  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. It is the value for very fine, artificial oxide at ordinary temperature, for very finely pulverized hematite, for hematite along the crystal axis, as well as for all the oxides above the Curie point. The different preparations at 20° gave widely differing values of  $\chi$ .

551. CHEVALIER, R., AND MATHIEU, S. [Variation in Magnetic Susceptibility of Hematite Powder With Size of Grains.] Compt. rend., vol. 204, 1937, pp. 854-856; Chem. Abs., vol. 31, 1937, p. 3352.

Three samples of hematite were separated, by powdering, sifting, and levigation in EtOH, into 9 samples

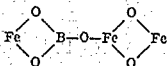
of different average diameters, 500-10 $\mu$ , and the magnetic susceptibility  $\chi$  of each was determined in a field of 700 gauss.  $\chi$  diminishes by about 10% as  $d$  decreases from 500 to 100 $\mu$ , then more rapidly to only about 25% of the initial value for  $d=10\mu$ . Extrapolated to  $d=0$ ,  $\chi=20-30 \times 10^{-6}$ , or approximately that of powdered artificial rhombohedral Fe<sub>2</sub>O<sub>3</sub>.

552. ———. [Adsorption in Precipitation of the Hydroxide From Ferric Sulfate.] Compt. rend., vol. 206, 1938, pp. 1249-1251, 1469-1471, 1955-1958; and vol. 207, 1938, pp. 58-61; Chem. Abs., vol. 32, 1938, pp. 4854, 5269, 6516.

In precipitating ferric oxide from a solution of ferric sulfate with KOH, the magnetic susceptibility of the precipitant is a strong function of the concentration and excess of base employed. The higher the concentration and excess of base, the higher the magnetic susceptibility of the precipitant. Studies conducted at the Bureau of Mines have shown that precipitated oxides prepared from ferric nitrate behave very similarly to the oxides studied above.

553. CHEVALIER, R., MATHIEU, S., AND GIRARD, J. [Monograph of Ferrous Boroferrite.] Bull. soc. chim., vol. 15, 1948, pp. 611-615; Chem. Abs., vol. 42, 1948, p. 7649.

Mixture of 2 gm. Fe<sub>2</sub>O<sub>3</sub> and 3 gm. Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, heated in a Pt boat at 1,000°, is reduced with either H<sub>2</sub> or CO; the cooled mass is treated with 3 N HNO<sub>3</sub>, and the residue is dried after being washed with hot H<sub>2</sub>O. Likewise the oxidation of a mixture of 2 gm. fine Fe and 4 gm. Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, heated in N<sub>2</sub> at 1,000° and oxidized with air, yields crystals of the boroferrite B<sub>2</sub>O<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub>·4 FeO. The product appears as fine black, opaque, orthorhombic crystalline needles. The boroferrite is readily attacked by dilute HCl, but less readily by H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>; the resulting solution shows properties of B<sub>2</sub>O<sub>3</sub>, Fe<sup>2+</sup>, and Fe<sup>3+</sup>. The constitution is believed to be



554. CHEVENARD, P. [Metallographic Interpretation of the Instability of Reversible Ferronickels.] Compt. rend., vol. 223, 1946, pp. 1074-1076; Chem. Abs., vol. 41, 1947, p. 3031.

Quenched ferro-Ni alloys show 2 stages of recovery. The 2d, starting about 300°, is accompanied by graphite precipitation and severe contraction. The 1st stage is, in general, an expansion effect from room temperature to 175°, but elongation-time curves show a contraction preceding the expansion. This is attributed to precipitation of cementite, favored by the Mn in the alloys, which subtracts Fe from the ferro-Ni and diminishes density. To suppress this instability, O should be held below 0.05%, remaining C should be stabilized with Ti or V, and the pieces should be treated before use to provoke all precipitation that can occur.

555. CHILTON, L. V., AND TOPP, N. E. Production of Mersol Products at I. G. Farbenfabrik, Wolfen. BIOS Final Rept. 1305, 1946, 7 pp.; PB 79,230.

Mersol is made by sulfochlorination of the hydrocarbon Mepasin (obtained by hydrogenation of Fischer-Tropsch Kogasin) using ultra-violet activation. Gives details of method. Petroleum hydrocarbons were not considered economically usable.

556. OHIWALA, A. [Formation of Mineral Oil by Chemical Interaction of Mineral Oil Hydrocarbons and the Synthetic Production of Derivatives.] Oesterr. Chem.-Ztg., vol. 48, 1947, pp. 2-6; British Abs., 1949, B, I, p. 238.

Review of interconversion of hydrocarbons by cracking and condensation, the formation of derivatives

from hydrocarbons by oxidation, chlorination, sulfochlorination and nitration, and the reaction of olefins with compounds containing hydroxyl, with HOCl, CO, and H<sub>2</sub> (catalytically), and with formaldehyde. The importance of these processes in the Austrian oil industry is considered.

557. CHLOSTA, J. [Wash-Oil Problem.] Oel u. Kohle, vol. 37, 1941, pp. 961-962; Chem. Abs., vol. 37, 1943, p. 6110.

Paraffin oils from brown-coal tar and low-viscous oils from the Fischer-Tropsch hydrocarbon synthesis process are both being successfully used for benzene scrubbing.

558. CHOUAT, G. [Residual Gas From Fischer-Tropsch Synthesis as Town's Gas.] Gas u. Wasserfach, vol. 83, 1940, pp. 497-499; British Abs., 1948, B, I, p. 64.

Composition of the gas varies rather widely, mean values being: CO, 17; CO<sub>2</sub>, 9; CH<sub>4</sub>, 33; H<sub>2</sub>, 20; N<sub>2</sub>, 20; C<sub>2</sub>H<sub>6</sub>, 0.7 volume %. The calorific value is within the town's gas range, but the high density and low flame speed render its behavior unsatisfactory unless it is mixed with not less than 2.5 volumes of normal town's gas.

See abs. 384.

CHOVIN, P. See abs. 2329.

559. CHIRSTESCO, J. [Procedure for Obtaining Synthetic Alcohols From Gas Mixtures.] Chaleur et ind., vol. 15, No. 167, 1934, pp. 456-458; Compt. rend. Cong. chauffage ind., 3d Cong., Paris, 1933; Fuel, vol. 14, 1935, pp. 23-25; British Chem. Abs., 1935, B, p. 259; Chem. Abs., vol. 28, 1934, p. 6423.

Method consists of bubbling a gas mixture through H<sub>2</sub>O at ordinary pressures in the presence of a catalyst. The experimental apparatus is pictured and described. Formation of MeOH from CH<sub>4</sub> is believed to take place as follows: CH<sub>4</sub>+H<sub>2</sub>O=CO+3H<sub>2</sub>; CO+3H<sub>2</sub>=MeOH+H<sub>2</sub>. A yield of 37% was obtained. EtOH was also prepared from gas mixtures. 10 refs.

560. CHRISTIANSEN, J. A. Equilibrium Between Methyl Formate and Methanol and Some Related Equilibria. Jour. Chem. Soc., 1926, pp. 413-421; Chem. Abs., vol. 20, 1926, p. 1745.

For the reaction 2H<sub>2</sub>+HCO.Me=2MeOH, log K<sub>298</sub> = -(3.016/T)+3.61 (over a range of 180°-240°); MeOH+CO=HCO.Me, log<sub>10</sub> K<sub>298</sub> = -(1.880/T)+4.82. For these values the reaction CO+2H<sub>2</sub>=MeOH is calculated: log K<sub>298</sub> = -4.896/T+8.43.

561. ———. Equilibrium Between Methanol and Its Decomposition Products. Jour. Am. Chem. Soc., vol. 52, 1930, p. 3165; Chem. Abs., vol. 24, 1930, p. 4981.

Christiansen's work was done in 1917-18, not in 1926.

562. CHRISTIE, J. J. German Chemicals Industry—Fischer-Tropsch Plants. Chem. Eng., vol. 57, No. 11, 1950, pp. 164-165.

Western Germany's 6 Fischer-Tropsch plants were removed from the reparations list for utilization of processes acceptable to the Allied Military Security Board. Already under way is the conversion of the Krupp-Treibstoffwerk at Wanne-Eickel to the Oxyl process. Work is being done by Lurgi in collaboration with Ruhrchemie A.-G. and is expected to be completed in the spring of 1951. It will have an output of 30,000 tons of alcohols per yr. The Oxyl synthesis (not to be confused with the Oxo process) is applied mainly to obtaining, in addition to hydrocarbons, alcohols with 2-40 C atoms. Alcohols and neutral oils are worked up and separated to yield primary alcohols with a purity of 95-98%, suitable for use as solvents or softeners or further processed into detergents. The synthesis gas used as the basic material differs from that used in the Fischer-Tropsch synthesis. Two catalysts are

used: A ferrous-based catalyst in the gaseous-reaction phase, and a Co-based catalyst in the liquid phase. The final products include approximately 17% gasoline, oils, and lubricants. It is proposed to convert the Bergkamen plant of Essener Steinkohlen A.-G. to production of gas for normal heating purposes by hyperpurification and detoxification of coke-oven gases. Proposals for conversion or disposition of the other 4 Fischer-Tropsch plants have not been announced. These plants are: Ruhrchemie A.-G. at Oberhausen-Holten, capacity 65,000 tons per year.; Steinkohlenberg werk Rheinpreussen at Moers, 73,000 tons capacity; Dortmunder Paraffin Werke of Dortmund, 50,000 tons capacity; Gewerkschaft Viktor at Castrop-Rauxel, 61,000 tons capacity.

CHU, P. L. See abs. 1269.

CHUFAROV, G. I. See abs. 3326, 3327.

563. CHUFAROV, G. I., AND ANTONOVA, M. F. [Retardation of the Bell Reaction 2 CO = C + CO<sub>2</sub>.] Bull. acad. sci. U. R. S. S., Classe sci. tech., 1947, pp. 351-359 (in Russian); Chem. Abs., vol. 42, 1948, p. 3648.

Decomposition of CO by the Bell reaction on an Fe catalyst is a 1st-order reaction over a pressure range 2-200 mm. CO and a temperature range 350°-750°, and obeys the equation  $-dp/dt = kp$ , where  $p$  is the pressure of CO. Over a temperature range of 350°-450°, the reaction rate changes according to the Arrhenius equation  $v = Ae^{-E/RT}$ , where  $E$ , the activation energy, is 34,000 cal. per mol. The addition of CuSO<sub>4</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, or MnSO<sub>4</sub> to the Fe catalyst causes a marked retardation of the reaction at a temperature around 450°, 5% of CuSO<sub>4</sub> or Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> completely inhibiting the reaction. The retardation is less pronounced at higher temperatures, but the effect is still large: at 650°-750°, 5% CuSO<sub>4</sub> retards the reaction by a factor of 40, whereas 5% Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> retards it by a factor of 12. More stable sulfates, Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, and CaSO<sub>4</sub>, are less effective in retarding the reaction. The inhibiting effect is caused by poisoning of the catalyst by the S-containing decomposition products of the sulfates, principally SO<sub>2</sub>.

564. CHUFAROV, G. I., AND AVERBUKH, B. D. [Initial Rate of Reduction of Hematite and Magnetite by Hydrogen.] Ztschr. physik. Chem., vol. B-33, 1936, pp. 334-348; Chem. Abs., vol. 31, 1937, p. 24.

Reduction of hematite and magnetite by H<sub>2</sub> was studied between 300° and 800° and at pressures between 0.1 and 0.001 mm. Hg. The autocatalytic nature of the reaction is satisfactorily explained by the formation of active centers during the course of the reaction. Above 600°, the lower rate as compared with that at lower temperature is due to recrystallization of these centers.

Reduction of Iron Oxides by Gaseous Reducing Agents. II. Rate of Reduction of Magnetic Iron Oxide by Hydrogen. See abs. 566.

565. CHUFAROV, G. I., AND LOKHIVITZKAYA, A. P. [Reduction of Iron Oxides by Gaseous Reducing Agents. I. Velocity of Reduction of Ferric Oxide by Hydrogen.] Jour. Phys. Chem. (U. S. S. R.), vol. 5, 1934, pp. 1103-1113; Chem. Abs., vol. 29, 1935, p. 3901.

Apparatus is described. Artificial and natural Fe<sub>2</sub>O<sub>3</sub> containing 98.6% Fe<sub>2</sub>O<sub>3</sub>, 0.35% Al<sub>2</sub>O<sub>3</sub>, and 1.1% SiO<sub>2</sub> were used. For both, an autocatalytic character of the speed of reduction by H<sub>2</sub> was revealed sharply. The 1st stage, reduction to magnetite, is not autocatalytic. The remaining stages, belonging to the type of inter-surface reactions, proceed autocatalytically. The anomalous course of the reduction curve above 600° is due to changes in the microporosity and ultramicroporosity of the solid product. The rates of reduction at temperatures 300°-900° are shown by a series of 11 graphs for various conditions of particle size, degree of pre-

vious reduction, etc. The porosity of the product is greater the lower the reduction temperature.

566. CHEFAROV, G. I., AND AVERBUK, B. D. [Reduction of Iron Oxides by Gaseous Reducing Agents. II. Rate of Reduction of Magnetic Iron Oxide by Hydrogen.] *Jour. Phys. Chem. (U. S. S. R.)*, vol. 5, 1934, pp. 1292-1298; *Chem. Abs.*, vol. 29, 1935, p. 5330.

Samples of magnetic iron oxide of natural origin and prepared from piano wire both show on reduction strongly autocatalytic effects. The initial speeds of reduction are greater the greater the temperature, 350°-900°, but above 600° the velocity of reduction falls off very quickly with time and the curve for 800° crosses that for 400° and 600° at about 70% reduction. Above 800° this effect again is less marked. Piano wire magnetite shows this effect much more pronouncedly than does natural magnetite. The micropore and ultrapore structures are also different on reduction. Reduction proceeds in 2 stages, first to FeO then to Fe. Most rapid, about 60 minutes. 90-100% reduction is obtained at about 600° C.

567. CHEFAROV, G. I., AND TATIEVSKAYA, E. P. [Reaction Zones in the Reduction of Magnetite and Hematite With Hydrogen.] *Acta Physicochim. U. S. S. R.*, vol. 3, 1935, pp. 957-974; *Chem. Abs.*, vol. 31, 1937, p. 4878.

Reaction is autocatalytic. The change in porosity with temperature and degree of reduction was studied and related to the reaction rate. Magnetite is less porous than hematite, but below 600° the rate of reduction is faster. Above this temperature the porosity and the rate of reduction decrease rapidly in both cases. Microscopical investigations show the presence of the layers  $\alpha$ -Fe-Fe<sub>2</sub>O<sub>3</sub> in the case of magnetite and  $\alpha$ -Fe-Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub> in the case of hematite, while FeO could not be detected, and it is suggested that Fe<sub>3</sub>O<sub>4</sub>→Fe is the rate-determining process. The rate of advance of the reduction zone is linear below 500° and the activation energy for hematite is 15,700 gm.-cal.

568. ———. [Comparison of Initial Velocities of Reaction of Oxides of Iron With Hydrogen and Carbon Monoxide and Their Mixtures.] *Jour. Phys. Chem. (U. S. S. R.)*, vol. 3, 1936, pp. 933-942; *Chem. Abs.*, vol. 31, 1937, p. 2075.

Near 500° the reduction of hematite is much slower by CO than by H<sub>2</sub>. At higher temperatures, 800°, the ratio of the velocities approaches the ratio of impinging molecules of the 2 gases. As a result of the smaller number of active centers at higher temperatures the absolute values of the reduction velocities are small. At 500° the presence of CO in mixtures of CO+H<sub>2</sub> decreases the reduction below that expected for the partial pressure of H<sub>2</sub> because of adsorption of CO on a large number of the active centers.

569. CHEFAROV, G. I., AND VILESOVA, G. F. [Influence of the Crystalline Lattice of an Oxide Upon the Speed of Reduction With Hydrogen.] *Teoriya i Prakt. Met.*, No. 4, 1936, pp. 10-17; *Chem. Abs.*, vol. 30, 1936, pp. 8115-8116.

Experiments were performed with grains of 0.5-1.0 mm. and with cubes of 5 x 5 x 5 mm. prepared from natural crystals of hematite and magnetite. Artificial oxides were prepared from piano wire. Reduction with H<sub>2</sub> was conducted at all possible temperatures up to 800°-900°. Above 600° the ultraporosity and microporosity of the magnetite reduction products is small. This blocks the penetration of the gas and the reduction is hindered. Below 600° the magnetite is sometimes reduced faster than the hematite. At higher temperatures the small crystal structure favors reduction, but at low temperatures it may hinder it because of its great adsorption of the reduction products.

CRNES, M. See abs. 828.

570. CLAR, —. [Improvement of Synthetic Oils by Means of Sulfuric Acid.] *FIAT Reel K23*, frames 2,381-2,391, Aug. 25, 1939; *PB 70,214*; *TOM Reel 290*. Experiments on the refining of synthetic oils with H<sub>2</sub>SO<sub>4</sub> have no success because of the undesirable side reactions, such as oxidation or formation of tar and esters. 7 tables.

571. ———. [Production of Oils From the Primary Products of the Gasoline Pressure-Synthesis.] *FIAT Reel K28*, frames 6459-6469, No. 26, 1940; *PB 70,185*; *TOM Reel 295*.

Preliminary treatment with NaHSO<sub>4</sub> + Na activated Al, SiCl<sub>4</sub>, ZnCl<sub>2</sub>, PCl<sub>5</sub>, and SnCl<sub>4</sub> of the gasoline produced under pressure leads to an increase in the oil yield with simultaneous formation of contact oil. Alcohols, which interfere with oil synthesis, are likely to be split into olefins and steam. When the gasoline vapors are passed over silica gel, isomerization is effected. Describes tests on a technical scale.

572. ———. [Lubricating Oil From Synthetic Gasoline.] *FIAT Reel K28*, frames 6120-6143, May 11, 1941; *PB 70,185*; *TOM Reel 295*.

Fractions of a cracked gasoline boiling within a narrow range and purified over metallic Na were used for the synthesis of lubricating oil. Comparison of the oils prepared from the fractions in a single synthesis shows an improvement in the viscosity-pole height and a deterioration of the Conradson test with increasing chain length while the aniline point and the I number decrease with rising molecular weight. A higher stability of the polymerizates obtained from C<sub>12</sub> and C<sub>14</sub> fractions, compared with those obtained from the C<sub>8</sub> to C<sub>10</sub> fractions, has been established by artificial aging. Acids, esters, and aldehydes are noxious; this is proved by the fact that after their elimination the viscosity-pole height and the Conradson test improve.

573. ———. [Density of Synthetic Oils and Its Dependence on the Nature of the Primary Gasoline and the Viscosity of the Oils.] *FIAT Reel K29*, frames 6,680-6,693, 1942; *PB 70,218*; *TOM Reel 296*.

Densities of a number of oil-test portions are tabulated according to their viscosities and their origins from cracked gasoline or from circulated gasoline. Their relations are represented graphically. Because of the large variation in the values, these curves do not have the significance of a functional relation but only of a correlation. As a rule, the densities of oils from cracked gasoline are higher than those of oils from circulated gasoline. Generally, density increases with increasing viscosity. 1 graph.

See abs. 3431.

CLARK, A. See abs. 19, 20, 1399.

574. CLARK, A., ANDREWS, A., AND FLEMING, H. W. Composition of a Synthetic Gasoline. *Ind. Eng. Chem.*, vol. 41, No. 7, 1949, pp. 1527-1532; *Chem. Abs.*, vol. 43, 1949, p. 7211.

8 fractions from a gasoline synthesized from CO and H<sub>2</sub> in the presence of a fluidized Fe catalyst of the synthetic NH<sub>3</sub> type at about 600° F. were percolated through silica gel. Each fraction was broken down into 4 types: Paraffins, olefins, aromatics, and oxygenated compounds. Some additional information was obtained on the character of the gasoline fractions. 40-50% by volume of the C<sub>8</sub>, C<sub>9</sub>, and C<sub>10</sub> fractions consist of straight-chain 1-olefins. 15 different aromatic compounds were identified as being present in the 1st 6 fractions. Evidence is fairly conclusive that small amounts of diolefins exist in most of the fractions.

575. CLARK, A. M. Large-Scale Production of Oxygen and Atmospheric Gases. *Bib. Soc. Ind. Repts.*, vol. 3, No. 3, 1946, p. 158; *BIOS Final Rept.* 591, 1946, 29 pp.; *PB 41,229*.

This report reviews the production of O<sub>2</sub> and other gases by the Linde-Frankl process. Altogether, 73 Linde-Frankl units have been erected by the Linde Co. since 1930, with an average capacity of 2,378 m.<sup>3</sup> per hr. of O<sub>2</sub> of 98% purity. The O<sub>2</sub> has been used mainly in the complete gasification of coal. Arrangement of plant and method of operation are described in some detail, with reference to the installation at Leuna. Analysis is made of available information relating to energy requirements of the process. Attempt also was made to determine the costs of O<sub>2</sub> production by the Linde-Frankl process.

It is claimed that O<sub>2</sub> can be separated from air at a purity of 98% with an energy consumption of 0.455 kw.-hr. per m.<sup>3</sup> of O<sub>2</sub>. The cost of production may vary between 1.6 and 3.0 pf. per m.<sup>3</sup> of O<sub>2</sub>, of which 40-50% may be accounted for by the cost of power. The capital cost of large installations appears to have been around RM 500,000 per 1,000 m.<sup>3</sup> per hr. of O<sub>2</sub> capacity. Gives flow diagrams.

CLARK, E. L. See abs. 2103.

576. CLARK, E. L., KÄLLENBERGER, R. H., BROWNE, R. Y., AND PHILLIPS, J. R. Synthesis-Gas Production. Reaction of Light Hydrocarbons, Steam, and Carbon Dioxide in Commercial Equipment. *Chem. Eng. Progress*, vol. 45, No. 11, 1949, pp. 651-654.

Production of synthesis gas of a wide range of H<sub>2</sub>:CO ratios in a Hyrgitol-type (Girdler Corp.) furnace is described. Operating data are presented for H<sub>2</sub>:CO ratios of 2:1 and 1:1. H<sub>2</sub> and CO mixtures containing 33-90% CO are produced by the reaction of natural gas (C<sub>1</sub>-H<sub>4</sub>) with steam and CO<sub>2</sub>. No trouble was encountered at any time with C deposition on the catalyst. The catalyst used was a Ni base catalyst furnished by the Girdler Corp. under the designation F-5. The product gas has such a low CO<sub>2</sub> content that its removal is not required, thus reducing plant-construction cost.

CLARK, G. C. See abs. 2061.

577. CLARK, R. H. Production of Liquid Fuels From Coal. *Canadian Min. and Met. Bull.* 190, February 1928, pp. 274-281.

This is a brief consideration of (1) production of primary tar by low-temperature carbonization; (2) hydrogenation of coal; and (3) Fischer-Tropsch process.

578. CLARK, W. New Synthetic Alcohol From Gasoline Is Developed for Plastics Industry. *World Petrol.*, vol. 20, 1949, pp. 44-45.

Development of the process announced by Esso Standard Oil Co. is reviewed. Iso-octyl alcohol is produced by the Oxo process, in which heptene from the polymerization of unsaturated cracker-gas reacts with CO-H<sub>2</sub> to form octanol. Hydrogenation of the latter at 3,000 p. s. i. gives principally C<sub>8</sub>-C<sub>9</sub> straight-chain alcohols with appropriate side chains. The octyl alcohols are in demand for the manufacture of plasticizers, particularly polyvinyl chloride.

578a. CLARKE, J., AND JACK, K. H. Preparation and the Crystal Structures of Cobalt Nitride, Co<sub>3</sub>N, of Cobalt Carbonylides, Co<sub>2</sub>(C, N), and of Cobalt Carbide. *Chem. and Ind.*, 1951, pp. 1004-1005; *Chem. Abs.*, vol. 46, 1952, p. 2948.

Co<sub>3</sub>N was prepared by passing anhydrous NH<sub>3</sub> over pure Co powder (380 mesh) at 350° with the partial pressure of H<sub>2</sub> kept at a minimum. A Co nitride approximating Co<sub>3</sub>N can be obtained by thermal decomposition of Co<sub>3</sub>N. CO at 340° gradually reacts with Co<sub>3</sub>N and Co<sub>2</sub>N to form the corresponding Co carbonylides. The Co<sub>2</sub>C of Hofer and Peebles (abs. 1440) is apparently identical with that prepared by the complete replacement of N in Co<sub>3</sub>N. X-ray powder photographs of Co<sub>3</sub>N, Co<sub>2</sub>C<sub>3</sub>N<sub>2</sub>, and Co<sub>2</sub>C show that

the unit-cell dimensions and the positions of the atoms within the unit cell change gradually as C replaces N. The space group is *D<sub>2h</sub>h*-*P m n n*. For Co<sub>2</sub>N the unit cell dimensions are a=2.8535, b=4.6056, c=4.3443 Å, and for Co<sub>2</sub>C, a=2.8969, b=4.4465, c=4.3707 Å.

579. CLARKE, G. [Present Situation With Respect to the Synthesis of Ammonia in Conjunction With Coke Ovens.] *Compt. rend.*, vol. 182, 1926, pp. 877-881; *Chem. Abs.*, vol. 20, 1926, p. 2229.

A phenomenon peculiar to this process and not previously described is the formation of MeOH during the conversion of CO (present as an impurity in the H<sub>2</sub>) to CH<sub>4</sub>, thus: CO+6H<sub>2</sub>→CH<sub>4</sub>+H<sub>2</sub>O. Up to 25% was found in the H<sub>2</sub>O of the reaction, having been formed by the reaction: CO+4H<sub>2</sub>→C<sub>2</sub>H<sub>5</sub>OH.

CLAUSMANN, P. See abs. 1168, 1169.

580. CLEMENT, —, AND DESORMES, —. Synthesis of Hydrocarbons and Alcohols From Water Gas. Specific Heat of Gases, Paris, 1802. In Marek and Hahn, *Catalytic Oxidation of Organic Compounds*, Chemical Catalog Co., New York, 1932, p. 101.

By passing steam over coke at red heat a combustible gas was produced analyzing as follows: H<sub>2</sub>, 56.22%; CO, 28.96%; CO<sub>2</sub>, 14.68%; CH<sub>4</sub>, 0.49%.

581. COAL AGE. Coal for Synthesis. Vol. 54, No. 1, 1949, pp. 66-67.

Brief review of development of a synthetic liquid-fuel industry and the part that coal is playing therein. It must not be assumed that natural and synthetic gaseous and liquid fuels are or will be capable of supplying the Nation's energy demands. Coal has its present competitive difficulties, but from the standpoint of reserves, availability, and cost it is in the best position of all fuels to undergo substantial expansion.

582. COAL CARBONISATION. Petroleum and Lubricating Oils From Coal. Vol. 1, 1935, p. 66; *Wärme*, vol. 38, 1935, p. 206.

Products of the Fischer-Tropsch process for making gasoline and lubricating oils from hard-coal coke are in no way inferior and in some ways superior to natural petroleum products. For example, the coldest of a good natural winter oil is -16° C. whereas that of a synthetic product is -42° C.

583. ———. Liquid Fuels in Germany. Vol. 3, 1937, p. 78; *Tech. moderne*, April 1937, p. 255.

4 plants are operating at Homberg, Castrop-Rauxel, Oberhausen-Holten, and Ruhland. The last-named plant has been enlarged to a capacity of 150,000 tons of oil per yr.

584. ———. Motor Fuels in Germany. Vol. 4, 1938, p. 65; *Bull. Hamburg World's Econ. Archiv.*, vol. 4, No. 6, 1938, pp. 88-90.

Review of factors that have influenced the development of substitutes for petroleum products in Germany. It is stated that 50% of the light fuel-oil requirements in 1936 were covered by home production, of which the Bergius and Fischer-Tropsch processes contributed 39%. These 2 processes are also of special importance in the domestic production of diesel fuel; the latter yields a high-grade, but rather expensive, diesel fuel. Bergius benzines are claimed to be superior to imported fuel as regards antiknock qualities, and further progress is expected from new catalysts. Benzines from Fischer-Tropsch process need cracking and blending to yield a satisfactory fuel. The Fischer-Tropsch process offers the special attraction of an outlet for semicoke from the low-temperature carbonization of coal.

585. COBURN, A. E. Liquid Gas and Coal. Fuel Oil and Oil Heat, vol. 6, No. 1, 1947, pp. 57-58, 148, 150; *Chem. Abs.*, vol. 41, 1947, p. 6385.

Sources of oil adequate for 1,000 yr. are seen in reserves of gas and coal for synthetic liquid-fuel processes. The use of  $O_2$  in gasification, the Lurgi process, underground gasification of coal, and the Fischer-Tropsch process are described briefly.

COCKS, L. V. See abs. 24.

COHEN, M. See abs. 2562.

COHEN, P. See abs. 740.

COHN, E. M. See abs. 52, 1436, 1437, 1438, 1439, 1445, 1446, 1447.

586. COHN, E. M., AND HOFER, L. J. E. Mode of Transition From Hägg Iron Carbide to Cementite. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 4062-4064.

Reaction of Hägg carbide,  $Fe_3C$ , to yield cementite,  $Fe_3C$ , and free C is a discontinuous or heterogeneous precipitation. Hägg carbide and cementite have narrow ranges of composition and apparently do not form intermediate metastable solid solutions. The reaction  $3Fe_3C-Hägg \rightarrow 2Fe_3C+C$  becomes appreciable only at about 450°, while the reaction  $Fe_3C-Hägg + Fe \rightarrow Fe_3C$  starts below 300°. The unstable or labile carbide of Kübel and coworkers is simply Hägg carbide.

587. CORTI, H. S., AND ROHRSCHEK, F. O. Determination of Suitability of Paraffin Mixtures for Conversion to Fatty Acids by Catalytic Oxidation. FIAT Final Rept. 903, Sept. 3, 1946; PB 42,659; Suppl. 1, 3 pp., TOM Reel 240.

Catalytic oxidation of paraffins to fatty acids is greatly dependent upon the characteristics of the raw materials, therefore small-scale tests are important for evaluating the proposed raw materials. 2 such tests are described and compared with the actual production procedure. One of the examples given is a paraffin mixture boiling 320°-450° (Fischer-Tropsch Gatsch) using potassium permanganate as catalyst. 3 German plants used this method: The I. G. plants at Oppau and Heydebreck and the Deutsche Fettsäurewerke at Witten. Supplement 1 contains 2 drawings of apparatus for oxidation.

587A. COKE. South African Coal-to-Oil Technical Plan. Vol. 13, 1951, pp. 385-390; Fuel Abs., vol. 10, No. 6, 1951, abs. 5,219.

Production at Coalbrook at initial rate of about 200,000 ton of liquid fuels a year will be based on a combination of improved German and American versions of the Fischer-Tropsch process. The cost percentage figures of the plant are: (a) Power station 19; (b) gasification plant 30; (c) fine purification plant 9; (d) synthesis reaction vessels 6; (e) distillation, polymerization, and other finishing plant for primary and secondary products, and storage facilities 24; (f) ancillary works installations 12. The coal of ash content about 26-29% will be gasified in a Lurgi pressure plant so that the gas is generated under the actual pressure needed for the synthesis. Ruhrchemie's experimental plant has given satisfactory results. Ruhrchemie-Lurgi "Restisol" process will probably be used for the gas purification.

588. COKE AND GAS. Fluidized Technique. Vol. 9, 1947, pp. 261-266.

Details of new technique developed by the American oil industry and its application to many industrial processes, such as oil cracking, Fischer-Tropsch synthesis, and retorting of oil shale.

589. Gasification Processes Compared. Vol. 9, 1947, p. 319; Rev. Gen. Gaz., vol. 69, No. 2, p. 44, 8 pp.

Summarizes information published in Germany in 1942 by Koppers concerning the complete gasification of lignite dust, coke fines, and the like. Particular attention is drawn to heat balances and cost data, and comparisons are made between the Koppers process

and conventional carbonization of coal in a coking plant followed by gasification of coke in gas producers. Heat balances are shown—one for the gasification of powdered lignite using  $O_2$ , for the production of synthesis gas, and the other without  $O_2$ . The gasification efficiency for each, respectively, is 86.9% and 74.5%. These figures compare with 68.8% for synthesis gas made by gasification of pulverized coal, details of which are given in the original article. Cost comparisons indicate that the conventional method is about 10% cheaper than the Koppers method in the manufacture of fuel gas; and when reduced to standard coking coal, the fuel consumption of the Koppers process per unit volume of synthesis gas is substantially higher than that of the conventional 2-stage process. Allowing for the indirect fuel consumption in the manufacture of  $O_2$ , the efficiency of the Koppers process is said to fall below 50%.

590. Iron Catalyst in the Fischer-Tropsch Synthesis. Vol. 9, 1947, pp. 125-127, 165-167.

Review of experiments carried out in Germany on the use of Fe catalyst in place of Co. The information was obtained mainly from papers already reviewed; such as BIOS Report 447, PB 77,705, CIOS Report XXXI-23, PB 12,624, and FIAT Reports 276, PB 1,291 and 420, PB 7,745. Developments sponsored by each of the following are presented: Kaiser Wilhelm Institute, Lurgi Gesellschaft, Braunkohle-Benzin A.-G., I. S. Farbenindustrie A.-G. (particularly the work of Michael on suspended catalyst, gas recycle, and catalyst for tubular reactors), Ruhrchemie, and Rheinpreussen.

591. Linde-Fränk Process for Oxygen Separation. Vol. 9, 1947, pp. 236-240.

Theory of air liquefaction is discussed and practical operating results are shown. A list of 73 units built between 1930 and 1941 is given. The working of the process is explained in some detail, and power requirements are calculated. Installation costs for early-war German conditions are given as RM 500,000/1,000 m.<sup>3</sup> of  $O_2$ /hour (English conversion rate RM 10 to 1 pound). Operating costs were divided for production up to 2,000 m.<sup>3</sup>/hr. into power 40%, amortization and 5%, interest 40%, and labor and material costs 20%. Above 2,000 m.<sup>3</sup>/hour the division was 50%, 40%, and 10%. In the plants with an hourly capacity of 1,000-2,000 m.<sup>3</sup> of  $O_2$ , the total cost of the gas was calculated to be 2.2-2.5 Rpfg./m.<sup>3</sup> at 0° and 760 mm.; in a 3,000-m.<sup>3</sup> plant the cost should fall to 1.5 Rpfg./m.<sup>3</sup>. A fair average cost figure/m.<sup>3</sup> of 98%  $O_2$  with power at 1.5 Rpfg./kw.-hr. would be 2.5 Rpfg. Converted into English equivalents, 98%  $O_2$  would cost 17 d./1,000 cu. ft. with power at 0.36 d./kw.-hr.

592. Manufacture of Primary Alcohols by the Oxo Process. Vol. 9, 1947, pp. 61-65.

Excellent review, with diagrams and flow sheets of the plant and operation, of the Oxo process for the manufacture of primary aliphatic alcohols from olefins and water gas. The information is adapted mainly from CIOS and BIOS reports. For the pilot plants at Holten (Ruhrchemie) and Leuna (I. G. Farbenindustrie, A.-G.) the cost of production of the alcohols was about RM. 0.90-0.95/kg. and the sales price RM. 2.5/kg. For large-scale production (12,000 tons batch process/year) the capital and operating costs were estimated at RM. 78/100 kg. of alcohol; for full-scale continuous operation RM. 60/100 kg. The potentialities of the process are briefly discussed from the viewpoint of products, and methods for increasing the production of olefins by medium-pressure, gas-recycle, and liquid-phase, fluid-catalyst are mentioned.

593. Production of Hydrogen-Carbon Monoxide Synthesis Gas From Coke-Oven Gas. Vol. 9, 1947, pp. 346-349.

Review mainly of information obtained from CIOS Reports XXV-7, PB 286, XXXIII-30, PB 28,745, XXVII-55, PB 368, and FIAT 513, PB 67,564. Describes processes employed by Hibernia, Klücknerwerke and I. G. Hoechst.

594. Synthesis of Higher Alcohols. Vol. 9, 1947, pp. 273-277.

Digest of the information found in CIOS reports XXX-103, PB 23,750, XXXII-96, PB 1,366, and XXXII-107, PB 6,650. It discusses the production of alcohols up to C<sub>6</sub> by the I. G. Farbenindustrie, the process of the Ruhrchemie A.-G. for alcohols above C<sub>6</sub> and, in particular, the Srol process of the I. G. Farbenindustrie. This process involves the reaction of a gas  $CO : H_2 = 1 : 0.7-0.8$  at 18-25 atm. and 180°-200° over a sintered Fe catalyst. The liquid products are mainly alcohols and hydrocarbons, the former being entirely straight-chain compounds; alcohols up to C<sub>6</sub> were made successfully. The process was never operated on a full scale.

595. Practical Advances in the Production of Liquid Fuels From Coal. Vol. 12, January 1950, pp. 9-17.

Account, with diagrams, of coal-to-oil demonstration plant at Louisiana, Mo.

596. COKE AND SMOKELESS-FUEL AGE. Diesel Fuels From Coal. Vol. 2, 1940, pp. 70-71; Ztschr. Ver. deut. Ing., vol. 83, No. 47, 1939, pp. 1240-1241.

Synthetic hydrocarbons of the Kogasin type, made by the Fischer-Tropsch process, have a cetene number of 120, and when about 38% is mixed with tar oil of 20 cetene number, a diesel fuel of 60 cetene number is obtained, which is equal in ignition qualities to commercial diesel oil of petroleum origin. Blended fuels must, however, be examined critically as regards miscibility, separation in storage, corrosive action, and coking qualities. Attempts to increase the ignitability of coal-tar oils by additions of ethyl nitrate and organic peroxides appear to have been abandoned for reasons of cost. H. Kübel claims to have developed stable diesel fuels from coal-tar oil and Kogasin, utilizing the selective solvent action of the latter to remove constituents liable to cause coking. The process is said to be applicable also to low-temperature tar oils. The latter have inherently higher cetene numbers. Data relating to a 45-55 Kogasin-coal tar-oil mixture show this to have properties better than those of an unnamed petroleum fuel. An illustration compares a mixture of this type with a commercial gas oil as regards: (a) Fuel consumption in gm./metric hp.-hr. (100 gm./metric hp.-hr. = 0.22 lb./hp.-hr.) in a 30- to 35-hp., 1,450-r. p. m., 4-cylinder engine; (b) exhaust temperatures; and (c) CO content of exhaust gases. The low CO content of the exhaust gases from the mixed fuel is specially interesting as it indicates the suitability of this fuel for use underground, in mine locomotives and the like.

597. Turbocompressors for Hydrogenation Plant. Vol. 2, 1940, p. 120; Génie civil, vol. 116, 1940, pp. 32-34.

Turbocompressors are lighter and more compact than reciprocating compressors for high pressures of the order of 200 atm. and offer the further advantage that the gas compressed does not come into contact with lubricating oil. The author discusses gas flow in labyrinth packings and methods of reducing the losses involved. The formation of eddies in the labyrinth and the magnitude of the leakage, with different sizes of chamber between the constrictions, were investigated by hydraulic experiments on a large-scale model.

598. Carbonization Research. Chemical Development. Vol. 5, 1943, pp. 151-153, 157.

Comments on an address by J. T. King before the Midland Association of Gas Engineers. The chemical development of coal utilization is likely to be based on the Fischer-Tropsch process. Gases containing CO and  $H_2$ , preferably in the ratio of 1:2, are purified from S to less than 0.1 grain per 100 cu. ft., and passed over a Co catalyst at temperatures between 175°-220° C. either at normal pressure or at 5-10 atm. Approximately 120 gm. of liquid product has been obtained per m.<sup>2</sup> gas treated at atmospheric pressure or 150 gm. at 10 atm. Yields are as follows, in percent by weight:

	Normal pressure	Medium pressure
CH <sub>4</sub> -----	18	11
C <sub>2</sub> +C <sub>3</sub> hydrocarbons-----	11	7
Oil below 200° C.-----	43	21
200°-320° C.-----	20	28
Wax-----	8	33

599. Reformation of Gas. Vol. 5, 1943, pp. 111-113.

Various processes (cracking in the water-gas machine, Linde's Eismaschinen, Kuhlmann, Koppers, I. G., and Kohletechnik) are described for the reformation of gas from coke ovens and low-temperature carbonization plants into synthesis and town gas.

600. Survey of German Low-Temperature Carbonization Technique. Vol. 5, 1943, pp. 68-72, 78, 84-88.

Although Germany had achieved considerable success in the low-temperature carbonization of brown coal, chiefly for the sake of the tar produced, the treatment of hard coal had been an economic failure until the development of the Fischer-Tropsch process. Hard-coal semicoke is used in quantity to make synthesis gas for the Fischer-Tropsch process, as it gives a smaller content of inerts and a better CO:H<sub>2</sub> ratio. The desired ratio can even be obtained by the gasification of some specially reactive semicokes. It is stated that the combination of low-temperature carbonization and the Fischer-Tropsch synthesis gives a 20-30% increase in the total yield of liquid fuels as compared with the more usual combination of high-temperature carbonization with the synthesis.

601. Syntheses From Carbon Monoxide and Hydrogen. Vol. 5, 1943, pp. 208-210, 215.

Survey of recent discoveries and historical sketch. Digest and translation of a paper by F. Fischer (abs. 972).

602. German Low-Temperature Carbonization. Vol. 8, 1946, pp. 77-79.

Technical details are given of the larger installations that were operated during the war in conjunction with synthetic-oil plants. Specially described are the plant of the Krupp Treibstoffwerke at Wanne-Eickel, operated in conjunction with a Fischer-Tropsch plant, the Lurgi Spüligas plants of the A.-G. Sächsische Werke at Böhlen, and Espenhain, and the Deutsche Erdöl A.-G. plant at Regis, all carbonizing brown coal chiefly to produce tar for the Bergius hydrogenation.

603. Lurgi Process. Vol. 8, 1946, pp. 49-50, 54.

Latest information about the Lurgi complete-gasification plant at Böhlen, Germany, reports a plant of 10 units, with a capacity of about 20,000,000 cu. ft. of gas per day. The complete plant cost 10,720,000 RM; the Linde-Fränk  $O_2$  plant 3,600,000 RM. Information is given on the modern type machinery and its operation, the gas-purifying plant, and an analysis of the fuel used. The consumption of materials per 1,000 cu. ft. of gas is:  $O_2$  145 cu. ft., steam 90 lb., coal 90 lb.; electricity 6-7 kw.-hr.; there 0.77 lb. of tar and 0.33 lb. of light oil are produced per 100 cu. ft. of gas. Oper-

ating costs are as follows: coal 6.50 RM per ton; water 6 pf. per m.<sup>3</sup>; power 1.1 pf. per kw.-hr.; labor and maintenance each 0.4 pf. per m.<sup>3</sup> of gas; oxygen 2.2 pf. per m.<sup>3</sup>. The total cost of the gas was 3.8 pf. per m.<sup>3</sup> less a credit of 1.4 pf. per m.<sup>3</sup>, or a net cost of 2.4 pf. per m.<sup>3</sup> or 10.9 d. per 1,000 cu. ft.

604. ———. Pintsch-Hillebrand Gasification Process. Vol. 8, 1946, pp. 218-220.

Pintsch-Hillebrand process is based on the use of heated circulating gas to supply the necessary heat for the reaction. Two plants are known: One at Hamburg gasifying brown-coal briquets and the other at the Wesseling hydrogenation plant of the Union rheinische Braunkohlen-Kraftstoff, which consists of 11 units, each of 5,500 m.<sup>3</sup> per hr. capacity, and uses brown-coal briquets with a pregasification shaft to drive off the tar. The construction and operation of the plant are illustrated and described, and operating results are tabulated. Since the plant was gravity operated, a very uniform fuel was necessary for efficient operation. The briquets were suitable if they had a specific gravity of 1.23, a moisture content of 13.5-14%, a strength of 140-180 kg. per cm.<sup>2</sup> (2,000-2,500 p. s. i.), and an ash-softening point of not less than 1,290°-1,300°. The gas produced was suitable for synthesis gas, having a CO : H<sub>2</sub> ratio of about 1 : 2.

605. ———. Thyssen-Galoczy Complete Gasification Process. Vol. 8, 1946, pp. 106-107.

Operating results of a 40-ton-per-day plant erected during the war at Wanne-Eickel. Due to the intermittent supply of O<sub>2</sub>, continuous operation for more than a few days was not possible, therefore results are not conclusive.

606. ———. Winkler Gasification Process. Vol. 8, 1946, pp. 155-158.

Winkler continuous gasification process, which uses a steam and O<sub>2</sub> mixture as the blast, is described, and its performance in various German plants is discussed. The great economic advantage of the process is its ability to gasify low-grade, cheap fuels. In fact this is its only compensatory feature for its relatively poor thermal efficiency and the inconvenience and cost of using O<sub>2</sub>. The capital cost of a Winkler plant is about the same as that of a complete water-gas plant of normal type.

607. COLBURN, A. P., DREW, T. B., AND WORTHINGTON, H. Heat Transfer in a 3 : 1 Hydrogen-Nitrogen Mixture at High Pressures. *Ind. Eng. Chem.*, vol. 39, 1947, pp. 958-964.

Experiments were conducted for flow inside a 5-ft. length of 3/8-in.-inside diameter steel tubing heated by steam, at gas pressures of 30-900 atm. The Reynolds numbers extend from 40,000 to the unusually high value of 440,000. The results are in good agreement with the usual relations for heat transfer. In the correlations the effects of pressure on the relevant properties of the mixture are taken into account. Methods of estimating these effects, which were not pronounced over the pressure range studied, are presented. Concurrence of the data with those for better known gases is shown by inclusion of experimental data for air at 5-S atm. and at Reynolds numbers from 9,000-50,000.

COLE, W. A. See abs. 178a.

608. COLLIERY ENGINEERING. Gasifying Run-of-Mine Coal. Vol. 20, 1943, pp. 237-238, 243.

Describes the Wintershall-Schmalfeldt gasification process in which synthesis gas is made from raw brown coal.

609. ———. Wintershall-Schmalfeldt Water-Gas Process. Vol. 23, March 1946, pp. 69-70, 72.

Description with diagram of the water-gas plant producing synthesis gas for the synthetic oil works at Lützkendorf. Raw brown coal is used containing

50-54% moisture. The plant comprises 4 gasifier units, each with a pair of generators and 5 producers. The output of synthesis gas under the best operating conditions is 1.07 million cu. ft. per hr. for each gasifier unit. Operation may be with or without O<sub>2</sub>; the usual synthesis-gas composition when using O<sub>2</sub> is CO, 25%; H<sub>2</sub>, 50%; CO<sub>2</sub>, 15%; CH<sub>4</sub>, 3.5%; N<sub>2</sub>, 3.5%. Without O<sub>2</sub>, the composition is 28%, 56%, 10%, 3%, and 3%, respectively. Gives some detailed operating results.

610. COLLIERY GUARDIAN. The Situation in Germany. Vol. 151, 1935, p. 581.

Capital cost of a Fischer plant is estimated at RM. 5,400 per metric ton of gasoline produced per day compared to RM. 4,000 for the L. G. coal-hydrogenation plant. Depreciation on the Fischer plant will, however, be less. The Fischer process will consume 7 tons of coke per ton of gasoline compared with 4 tons of coal for the coal-hydrogenation process.

611. ———. Production of Oils From Coke-Oven Gas—Report of Utilization of Coal Committee. Vol. 153, 1936, pp. 380-381; *Inst. Min. Eng.*, Mem. 19, August 1936, p. 2.

Outline of the Fischer-Tropsch process, with special reference to the modification by Fischer, Pichler, and Köhler, whereby a suitable synthesis gas is produced by blowing a water-gas generator with a mixture of steam and coke-oven gas. For example, if 10 cu. ft. of coke-oven gas were used for every pound of steam, the resulting gas would have a composition % by volume: H<sub>2</sub>, 60; CO, 30; N<sub>2</sub>, and other gases, 10. For each 1,000 cu. ft. of this gas, 330 cu. ft. of coke-oven gas and 18 lb. of steam were used.

612. ———. Developments in South Africa. Vol. 156, 1938, p. 329.

Local rights in the Fischer-Tropsch process have been granted to the South African Torbanite Mining & Refining Co.

613. ———. Fischer-Tropsch Process. Production of Coal Spirit and Its Improvement by Cracking. Vol. 156, 1938, pp. 483-484.

In this process a mixture of CO and H<sub>2</sub> in the ratio of 1 : 2 by volume is used. Ordinary water gas, produced by passing steam over coke, seems to be the most economical source of synthesis gas. To make up the deficiency of H<sub>2</sub> in water gas, the producer operation is modified by operating at a low temperature or by treating the water gas with steam. The synthesis gas is treated in a 2-stage purification plant for the removal of S. The 1st stage is the usual gas-works practice at normal temperatures, and the 2d stage is the removal of organic S at elevated temperatures. Purified gas must contain less than 0.2 gm. of S per 100 m.<sup>3</sup>. The catalyst is a Co salt distributed on a kieselguhr foundation. The reaction takes place in 2 stages, and the temperature and pressure must be carefully controlled. The heat released by the strongly exothermic reaction is immediately removed by the production of steam at constant temperature and pressure. The gas leaving the condensing equipment passes through an activated C absorption plant for recovering volatile oils. The theoretical yield figure is approximately 170 gm. of hydrocarbons per m.<sup>3</sup> of synthesis gas. 2 years ago the yield stood at 100-150 gm. per m.<sup>3</sup>, but this has been increased and is now stated to have reached the figure of 120-130 gm. per m.<sup>3</sup>. Part of the product must be cracked in order to reduce the knocking properties of the fuel.

614. ———. Fischer Process, France. Vol. 159, 1939, p. 170.

Report presented by the Société des produits chimiques Courrières-Kuhlmann, a subsidiary of the Mines de Courrières and établissements Kuhlmann, mentions that in 1938 the plant for the production of

synthetic fuel contributed for the first time to the profits. The plant uses the Fischer-Tropsch process and the regular output is 30 tons of synthetic petroleum for every working day. The capacity may enable a doubled production. This installation is the only one in France that was installed and that is run without any financial assistance from the State, and the production proves beneficial. It is protected by the almost prohibitive duties imposed on all imported petroleum.

615. ———. Motor Fuels. Vol. 159, 1939, p. 727.

Australian Commonwealth Standing Committee on Liquid Fuels reports that the Government should exhaust the possibilities of accumulating large quantities of gasoline in storage and the production of other substitute fuels before embarking on the establishment of either hydrogenation or synthesis plants. The cost of producing gasoline by hydrogenation or synthesis from either bituminous or brown coal would be about 1 s. 4 d. per gal. A synthesis plant of 18,000,000 gal. per yr. capacity would cost pounds 5,000,000 and a hydrogenation unit of 45,000,000 gal. per yr. capacity pounds 12,000,000. It is estimated that the cost to the consumer of synthetic gasoline from Victorian brown coal would be 2 s. 1 d. per gal.

616. ———. Oil From Australian Brown Coal. Vol. 158, 1939, pp. 88-89; *British Coal Utilisation and Research Assoc.*, Monthly Bull., vol. 3, No. 1, Abs. 3042.

In a report to the Victorian Government regarding the production of oil from brown-coal deposits, it is stated that the cost would be about 1 s. per gal. The cost of the plant would be about pounds 4,000,000 based on a 60,000-ton unit. It is thought that the costs could be reduced considerably if the oil is produced in conjunction with the existing electricity and briquet works. The scheme, which has been prepared by German experts, embodies many improvements enabling the proposition to be placed on a commercial basis to suit Victorian conditions, and the cost of production is much lower than any previously published figures. The report covers both the Fischer process, which is highly mechanized and involves low labor costs, and coal hydrogenation, which is at present producing greater quantities of oil.

617. ———. Production of Oil From Coal by the Fischer-Tropsch Process. Vol. 158, 1939, pp. 865-868.

Reviews history of Fischer-Tropsch process and discusses temperature control, catalysts, and fuels used in the production of the synthesis gas. It is possible to produce synthesis gas immediately from coke-oven gas by suitable treatment in a cracking plant. At the same time, the heating of coke ovens by low-grade gas is promoted, the coke-oven gas being used for the production of motor fuel while the CO, necessary for the conversion of the coke-oven gas can be produced from the waste gases of a coke-oven battery heated by blast-furnace gas, as this waste gas is free from S compounds because the blast-furnace is free from S. The coke-oven gas is freed from H<sub>2</sub>S before its conversion, and the finished synthesis gas, therefore, only needs to be freed from organic S compounds. Alternatively, coke-oven gas can be transformed in a cracking plant with water gas, the latter being produced in a water-gas plant by the gasification of coke with O<sub>2</sub> and steam continuously. The Fischer-Tropsch process has been operated recently at pressures around 10 atm. In this way, the yield has been increased about 25-30%, mainly owing to an increase in the paraffin yield. This operation is now known as "medium-pressure synthesis" and the gas and contact material used are exactly the same as those used for normal-pressure synthesis. Below a pressure of 20 atm. there is no appreciable formation of oxygenated compounds such as fatty acids. With the medium-pressure synthesis,

the catalyst has a considerably longer life than with the normal pressure operation, in fact as much as 7 times as long. The products obtained by this new method are not used directly either as motor or Diesel fuels but are cracked or polymerized by well known and existing methods. The condensable hydrocarbons consist mainly of propane-butane mixtures and are similar in composition to the Calor gas sold in this country for country-house lighting and heating. The octane number of the Fischer-Tropsch motor spirit is similar to that of straight petrol, as would be expected from the similarity in composition. The olefins from the Fischer-Tropsch process produce lubricants of a very high grade. They are adjustable to such an extent that lubricating oils suitable for any purpose whatever can be produced synthetically.

618. ———. Robinson-Bindley Process. Vol. 159, 1939, p. 203; *Chem. Trade Jour.*, vol. 104, 1939, p. 200.

Synthetic Oils, Ltd., has issued a report on a test run of the company plant at Bedlay for producing hydrocarbon oils from blue wafer gas. The test substantiates the results obtained by the company's technicians in a pilot plant at the research station at Epsom. According to the report, the yield of oils during the trial was equivalent to 0.501 gal. for every 1,000 cu. ft. of gas put through the plant, but a new method has just been devised that should bring the yield up to more than 1 gal. per 1,000 cu. ft. of gas throughput. It appears from the report that several programs of treatment of crude oils can be employed, which would mean that the products could, to some extent, be varied so as to meet current market conditions. The amounts of motor spirit, diesel, and other oils that can be produced from the crude oil are somewhat similar to those obtained from natural petroleum, but the quality of some of the oils is much better. One program of treatment mentioned in the report shows that nearly 30% of the total crude products can be converted into motor spirit and 40% into diesel oil, and by another program, nearly 40% of motor spirit and more than 40% of very high-class kerosene can be obtained. The motor spirit contains only 0.09% S, which is well within the Air Ministry's requirements. Moreover, the actual and potential gum is less than half that stipulated in the Air Ministry's specification for aviation fuels. The motor spirit, after certain normal and well established treatment, compares most favorably with No. 1 grade motor spirits. The diesel oil and kerosene are said to be vastly superior to any such oils on the market. Lubricating and transformer oils can be obtained also from the synthetic crude oil. It was found after the trial that the activity of the catalyst had not been impaired.

619. ———. German Fischer-Tropsch and Allied Processes. Vol. 172, 1946, p. 589.

Brief review of information digested from the CIOS reports on process development in the Fischer-Tropsch synthesis. The Lurgi Gesellschaft had been given all rights for the construction of future plants, and their research staff had developed and patented the recirculation of synthesis gas, pressure gasification, and the use of Fe catalysts. The advantages are stated to be: higher gas velocity and easier heat control; no hydrogenation of olefins to paraffins; and suppression of cracking by the high CO : H<sub>2</sub> ratio, giving less CH<sub>4</sub> and less C.

619a. COLTIER, O. A., AND JONKARD, A. Aliphatic Chemicals. *Advances Chem. Ser. 5*, 1951, pp. 287-298; *Chem. Abs.*, vol. 45, 1951, p. 10,560.

Developments of the past 25 yr. are reviewed. Among the more recent developments are the direct oxidation of hydrocarbons to produce aldehydes, acids and alcohols; partial combustion of CH<sub>4</sub> to produce C<sub>2</sub>H<sub>2</sub>; and

the Fischer-Tropsch and Oxo synthesis to yield oxygenated chemicals.

COMAFORD, D. J. See abs. 1195.

620. COMBUSTION. Fischer-Tropsch Process in United States. Vol. 14, No. 2, 1942, p. 44.

New research has been authorized by Congress. This process has certain advantages over the Bergius process. The output of the latter is a liquid that requires further refining, whereas the Fischer-Tropsch process yields a number of separated fuel and lubricant products directly. It also requires less precision machinery and is economically practicable in smaller units, about 30,000 tons annually compared with 150,000 tons for the Bergius process. Both processes yield about 1 ton or between 250-300 gal. of liquid products from 4-5 tons of coal.

621. COMPAGNIE GÉNÉRALE CONSTRUCTION FOURN. [Experimental Station for Production of Town Gas and of Synthesis Gas From Lignites of Faveau Basin.] Cahier S1; Fuel Abs., vol. 5, abs. 4703, 1940.

This plant at Digoïn consists of 1 full-scale unit of Woodall-Duckham continuous vertical retorts. The lignite contains 8.5-9% moisture, 14.4% ash, 46% volatiles, and 54% fixed C on the dry ash-free basis. When making synthesis gas the central-gas offtake was used. The production of town gas was 350 m<sup>3</sup>/hour ton or 12,560 cu. ft./ton at 4,000 calories or 420 B. t. u./cu. ft. The production of Syngaz was 1,030 m<sup>3</sup> or 36,950 cu. ft./ton at 2,900 calories or 300 B. t. u./cu. ft. The Syngaz was required to have a ratio CO : H<sub>2</sub> = 2 : 1 and as little CH<sub>4</sub> as possible. The composition of town gas was: CO, 25.7%; H<sub>2</sub>, 39.4%; and CH<sub>4</sub>, 16.3%. The composition of Syngaz was: CO, 27.0%; H<sub>2</sub>, 54.2%; and CH<sub>4</sub>, 3.2%. This satisfactory result is attributed to the central offtake giving maximum cracking of CH<sub>4</sub> and an increase in steaming from 8 to 32%.

622. CONNANON, C. C. AND SWIFT, A. H. World Chemical Developments in 1937. U. S. Department of Commerce, Bureau of Foreign and Domestic Commerce, Trade Promotion Series 177, 1938, pp. 52-53.

In 1937, Germany was able to supply over one-half of its requirements of light motor fuel from domestic sources. 3 large new synthetic-gasoline plants were brought into production, and 10 smaller ones were constructed. The 1st large-scale commercial plant for producing synthetic fatty acid by the oxidation of paraffin hydrocarbons began operations in the latter part of 1937 with a capacity of 20,000 metric tons/yr.; 2 additional plants of like capacity are under construction. When in full operation these 3 plants will supply 25% of the soap industry's requirements of fatty acid, estimated at 250,000 tons.

623. CONWAY, J. J. Equipment for Low-Cost Oxygen Production. Petroleum Meeting, Am. Soc. Mech. Eng., Tulsa, Oct. 7, 1946; Petrol. Processing, vol. 2, 1947, pp. 113-114; Petrol. Refiner, vol. 26, No. 6, 1947, pp. 557-561.

Process developed by Hydrocarbon Research, Inc., for production of O<sub>2</sub> and the 2,000-ton/day plant now under construction as part of the synthetic fuel installation of Carthage Hydrocol at Brownsville, Tex., are described. The plant will provide 48,000,000 cu. ft. of 95% purity O<sub>2</sub>/day at a cost of \$0.05/1,000 cu. ft., including amortization in 15 yr., maintenance at 2% of the capital investment, and operating labor at \$2.00/hr., but excluding power and water costs as these are both by-products of the process. O<sub>2</sub> is separated from the air by new developments that treat the air as a binary mixture of N<sub>2</sub> and O<sub>2</sub>, removing the latter by fractionation. The operations involved consist essentially of compression, heat exchange, refrigeration, and fractionation, as shown by a flowsheet. An estimate of the proportional effect of certain major cost items on the cost of manu-

factured O<sub>2</sub> is indicated. It is seen that a power cost of \$0.05/kw.-hr. accounts for about 65% of the cost of O<sub>2</sub>. The advent of cheap O<sub>2</sub> opens up possibilities for its large-scale use in 6 fields: Partial oxidation of hydrocarbon gases; gasification of coal; heavy chemical industries; iron and steel manufacture; nonferrous metal industry; and mining.

CONWAY, M. J. See abs. 1619.

624. COOK, G. A. Possibilities of Power Alcohol and Certain Other Fuels in Australia. Australia Council Sci. Ind. Research, Bull. 33, 1927, pp. 7-106; Chem. Abs., vol. 22, 1928, p. 492.

Possibilities are discussed of manufacturing EtOH in Australia from cellulosic materials: Sawdust, wood, sulfate waste liquors, and straw husks. Describes the known processes of making EtOH from C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>MeOH from CO+H<sub>2</sub> and the Synthol and Synthin of F. Fischer.

625. COOPERMAN, J., DAVIS, J. D., SEYMOUR, W., AND RUCKES, W. L. Lurgi Process for Complete Gasification of Coals With Steam and Oxygen Under Pressure. Bureau of Mines Bull. 498, 1951, 38 pp.

An investigation was made, in an apparatus closely simulating that used in industrial-scale operation, to determine the proper fuels and operating conditions to be used in carrying out the Lurgi process of gasification. It was found that caking coals cannot be gasified, but noncaking fuels, such as anthracite and low- and high-temperature cokes can be completely gasified in a Lurgi apparatus with the production of a CO-free fuel gas of about 410 B. t. u./cu. ft. heating value. Low-temperature coke or char can be made from bituminous coals in various ways, particularly in batches in a rotating retort. By passing the Lurgi gas, properly purified from S, over a Ni methanization catalyst, a synthesis gas of about 950 B. t. u./cu. ft. was obtained after scrubbing out the CO<sub>2</sub>. The catalyst was the British Gas Research Board type made by precipitating 100 parts by weight of Ni(NO<sub>3</sub>)<sub>2</sub> · 20 Mn(NO<sub>3</sub>)<sub>2</sub> · 13.6 Al(NO<sub>3</sub>)<sub>3</sub> · 25 china clay with 97 K<sub>2</sub>CO<sub>3</sub> and reducing for 2 hr with H<sub>2</sub> at 400° and 300 p. s. i. Diagram and flow sheet of the apparatus are shown.

COQUELLE, O. See abs. 189.

626. CORCORAN, W. H., ROUBINEUSH, B., AND SAGE, B. H. Temperature Gradients in Turbulent Gas Streams. Preliminary Studies. Chem. Eng. Progress, vol. 43, 1947, pp. 135-142.

Equipment is described that permits measurement of the temperature and velocity distribution in an air stream with essentially 2-dimensional flow characteristics. Preliminary results, including data describing the temperature and velocity distribution, heat transfer from the wall, and shearing stress, are submitted for 7 different sets of conditions. The data indicate that, within the accuracy of measurement, the eddy viscosity and eddy conductivity are equal, as was assumed by von Karman in his analogy between the transfer of momentum and the thermal transfer of energy. The over-all heat-transfer rate predicted by the Karman analogy agrees with the experimental results in the case of a symmetrical temperature distribution. However, significant divergences from the heat-transfer rates predicted by the analogy were experienced in the case of nonsymmetrical temperature distributions. The results presented are of a preliminary nature and not of sufficient extent to permit the experimental uncertainty to be established definitely. The detailed study of temperature and velocity distribution together with the associated heat transfer and shearing stress permits a microscopic evaluation of the thermal transfer of energy through a turbulently flowing air stream. The methods employed appear to be capable of refinement, and further study of thermal transfers of energy by these and related methods should permit ultimately

the more accurate prediction of the rate of thermal transfers of energy for situations where the transfers of momentum can be predicted from the science of fluid mechanics.

CORDNER, J. B. See abs. 3305a, 3306.

COREY, R. C. See abs. 810a, 2615.

627. CORNUAULT, P. [Adsorbed Phase on Catalysts.] Jour. chim. phys., vol. 47, 1950, pp. 157-164; Chem. Abs., vol. 44, 1950, p. 8213.

Kinetics of desorption of H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> from a Ni-Al-Mn-kieselguhr Fischer-Tropsch catalyst reduced in H<sub>2</sub> at 475° was measured on a sample (I) sealed off at 450° immediately after reduction, on one (II) cooled from 475° to 175° and maintained 4 hr. in H<sub>2</sub> at this temperature, and on one (III) kept 113 hr. in H<sub>2</sub> at 175°. Evolution of gas from (II) with increase of temperature is very similar to that from (III). The energy of activation of desorption up to 200° is about 19 kcal. On both samples (II) and (I), the energy of activation of desorption is about 29 kcal. at 450° Evolved gas contained 73-100% H<sub>2</sub>; the other components were small amounts of CO<sub>2</sub>, CO, and CH<sub>4</sub>, coming from undecomposed carbonates of the original catalyst. Composition of the gas evolved at each temperature is given for all samples.

CORRELLI, R. See abs. 1135.

CORRIGAN, T. E. See abs. 144a.

628. CORSON, B. B. Industrial Catalysis. Jour. Chem. Education, vol. 24, 1947, pp. 150-155.

Nontechnical account of synthesis of gasoline and MeOH by the Fischer-Tropsch reaction.

629. CORTON, E. Germany's Fischer-Tropsch Process. Summary of Latest Developments and Operating Procedures. Nat. Petrol. News, vol. 38, No. 23, 1946, pp. R425-426, 428, 430, 432-434; Chem. Abs., vol. 42, 1948, p. 9112; PB 12,618, 1946, 16 pp.

Summary of the investigations by United States Technical Oil Mission. Discusses the commercial methods of preparing and purifying synthesis gas by the water-gas process and the CH<sub>4</sub>-O<sub>2</sub> process; the preparation of the standard Co catalyst (100Co-5ThO<sub>2</sub>-5MgO-180-200 kieselguhr) by precipitation from the nitrates and its reduction in a stream of gas (75H<sub>2</sub>-25N<sub>2</sub>) at 400° and a space velocity of 8,800 for 40-60 min.; the type of reactors employed for both the normal and medium-pressure processes; and the actual synthesis procedure and the products obtained. Also included is some information on the gas recycle operation and some details of the development of the Fe catalyst. The latter is made by pasting Fe powder prepared by thermal decomposition of Fe carbonyl with 1% of borax and forming into approximately 1-cm. cubes, which are sintered and reduced with H<sub>2</sub> at 800°-850° for 4 hr. An interesting development in the use of the Fe catalyst is the hot-gas recycle process in which gas is circulated over the catalyst and through a cooler at such a rate that the temperature rise in the catalyst bed is limited to a maximum of 10°. The reaction is carried out at a pressure of 300 p. s. i. with a gas-recycle ratio of 100 vol. of recycle to 1 vol. of fresh feed; contact time in the catalyst bed is approximately 0.5-1 sec./pass, with a gas velocity of about 1 m./sec. Another interesting development in the use of the Fe catalyst is the fixed-bed, oil-circulation process by which the heat of reaction is removed by circulating a product cut of fixed boiling range over the catalyst. The heat is removed by raising the temperature of the oil as well as by partial vaporization of the oil. The process operates at 20-25 atm. and 250°-300° in the first stage and 280°-330° in the second stage. Synthesis gas with a ratio of CO : H<sub>2</sub> = 55 : 45 is used. The throughput is controlled to yield 20-25 gm. of total product/l. of

catalyst/hr. The catalyst is the same as that used in the hot-gas recycle process.

COWDRAY, R. See abs. 2720, 2721.

COUTFAIK, F. See abs. 3187.

630. COTRY, C. [Study of Adsorption Phenomena by Means of a Weak Magnetic Field.] Proc. Pure Applied Chem. Internat. Cong. (London), vol. 11, 1947, pp. 397-409 (in French); Chem. Abs., vol. 44, 1950, p. 5166.

Review with 40 refs.

631. ———. [Magnetic Measurements Applied to Adsorption.] Compt. rend., vol. 230, 1950, pp. 745-747; Chem. Abs., vol. 44, 1950, p. 5061.

Adsorption of H<sub>2</sub>O and air on activated charcoal was studied by measuring the magnetic susceptibility of the adsorbent containing air and H<sub>2</sub>O. The value for pure H<sub>2</sub>O, -0.72 × 10<sup>-6</sup>, was found constant for adsorbed H<sub>2</sub>O also. The value for air, +2.16 × 10<sup>-6</sup>, decreased slowly to +1.94 × 10<sup>-6</sup> at 20°.

632. ———. [On the Evolution of the Magnetic Properties of Oxygen Adsorbed on Activated Charcoal Which Has been Activated in a Vacuum at Elevated Temperatures.] Compt. rend., vol. 230, 1950, pp. 1588-1589; Chem. Abs., vol. 44, 1950, p. 10, 403.

The coefficient of magnetization was calculated for O<sub>2</sub> adsorbed on charcoal activated in a vacuum and at elevated temperatures. This same measurement had been previously carried out on charcoal activated in a vacuum in the cold. In this experiment the charcoal was activated in a vacuum of 0.02 mm. for 6 hr. at 900°. When this charcoal was put into contact with O<sub>2</sub>, the adsorption was accompanied by the release of a great amount of heat, 5.6 cal. This was attributed to the formation of CO<sub>2</sub>. It was found that the decrease in the paramagnetism is of the same order for C that has been activated either in the cold or at high temperatures.

COUTSEMANT, F. See abs. 1648.

COWAP, M. D. See abs. 2304, 2305.

COWARD, H. F. See abs. 292, 293, 294.

633. COWARD, H. F., AND WILSON, S. P. Equilibrium in the System Carbon, Hydrogen, and Methane. Jour. Chem. Soc., vol. 115, 1919, pp. 1380-1387. Chem. Abs., vol. 14, 1920, p. 1521.

Synthesis of CH<sub>4</sub> from its elements was achieved by Bone and Jordan (abs. 296) and confirmed by Bone and Coward (abs. 293); the decomposition of CH<sub>4</sub> into C and H<sub>2</sub> was demonstrated by Bone and Coward (abs. 294). Equilibrium in the system C + 2H<sub>2</sub> = CH<sub>4</sub> at 1,000°-1,200° showed that the mixture contained approximately 1% of CH<sub>4</sub>. The present experiments were carried out in the apparatus described by Bone and Coward, the gaseous products being passed several times through the heated porcelain tube until analysis indicated that equilibrium was reached. The % compositions of the equilibrium mixtures of CH<sub>4</sub> and H<sub>2</sub> were respectively: At 1,100°, 0.6 and 99.4; at 1,000°, 1.1 and 98.9; at 850°, 2.5 and 97.5. Calculation of the heat of combustion of CH<sub>4</sub> from the experimental values, using the integrated form of the equation  $d \log K/dT = -Q/RT^2$ , gives 18,000 cal., with a possible error of 2,000 cal. Equilibrium was reached both by synthesis and decomposition. The use of Ni or Pt as catalyst was advantageous at the lower temperatures, the gases showing practically constant composition after the 2d passage. A steady production of CO was noted, due to a side reaction between H<sub>2</sub>O vapor and C.

634. CRANE, J. E. Development of the Synthetic Ammonia Industry in the United States. Ind. Eng. Chem., vol. 22, 1930, pp. 795-799; Chem. Abs., vol. 24, 1930, p. 4359.

Data are also given on the production, cost, and use of synthetic MeOH.

635. CRANGLE, J., AND SUCKSMITH, W. Magnetic Analysis of Iron-Carbon Alloys. Tempering of Martensite and Retained Austenite. Jour. Iron Steel Inst. (London), vol. 198, 1951, pp. 141-151; Chem. Abs., vol. 45, 1951, p. 6359.

Pure Fe-C alloys were austenitized and quenched to convert them to martensite. Magnetic analysis indicates that hexagonal Fe carbide is present in the 1st tempering stage (100° C.); its Curie point may be considerably lower than 350° C., and its composition may differ from Fe<sub>3</sub>C. The 2d tempering stage (150°-200° C.) is characterized by the absence of retained austenite (which decomposes into the same products that were formed in the 1st stage) and by the appearance, above 200° C., of a small amount of cementite. The shapes of the thermomagnetic curves of specimens in the 3d stage (250°-350° C.) suggest the presence of a carbide with properties similar to Hägg carbide. To eliminate this carbide completely, the temperature must be raised above 500° C. where the only remaining carbide is cementite.

CRAWFORD, R. M. See abs. 2154, 2155.

636. CRAWFORD, V. A., AND TOMPKINS, F. C. Adsorption of Gases Sulfur Dioxide, Ammonia, Carbon Dioxide, and Nitrous Oxide on Barium Fluoride Crystals. Trans. Faraday Soc., vol. 44, 1948, pp. 695-708; Chem. Abs., vol. 43, 1949, p. 2485.

Adsorption was determined between -78° and 119°, and it was reversible and complete within 5 min. of gas admission at all temperatures. The Brunauer-Emmett-Teller plots are linear except at low pressures ( $p$ ), where departures were anticipated. The volume adsorbed tends to be too small at high pressure ( $p$ ), in keeping with the decrease in the heat of adsorption. The latter was determined by use of the Clausius-Clapeyron and the B. E. T. equations. The decrease of heats with coverage found by experiment is compared with those expected theoretically. Variation in adsorption potential over the crystal surfaces was calculated in an approximate manner and the significance discussed from the viewpoint of the applicability of the B. E. T. multilayer theory.

637. CRANFORD, S. R. Reactions of the Fischer-Tropsch Process. Fischer-Tropsch Synthesis of Hydrocarbons and Some Related Reactions. Trans. Faraday Soc., vol. 35, 1939, pp. 946-958, 966-967; Brennstoff-Chem., vol. 20, 1939, pp. 263-270; British Chem. Abs., 1939, B, p. 1097; Chem. Abs., vol. 33, 1939, p. 9606.

At the temperature of the Fischer synthesis (~200°) CO reacts slowly with the catalyst to form Co<sub>3</sub>C, but this reaction is always slower than the reduction of the Co<sub>3</sub>C by H<sub>2</sub> at the same temperature. With CO and H<sub>2</sub> the catalyst forms Co<sub>3</sub>C+H<sub>2</sub>O and this reaction is faster than the reduction of the carbide by H<sub>2</sub> under the synthesis conditions. When oils are produced by the Fischer synthesis, the *o-p*-H<sub>2</sub> conversion is inhibited; when CH<sub>4</sub> is the product of the synthesis, the *o-p*-conversion occurs freely. This shows the presence of chemisorbed H on the catalyst surface in the latter case but not in the former. The water-gas reaction runs parallel to the *o-p*-H<sub>2</sub> conversion. It is inhibited during oil formation as is also the hydrogenation-cracking of paraffin hydrocarbons on the catalyst. Theoretical deductions are made starting with the assumption that the first step in the synthesis is the alternate formation and reduction of Co<sub>3</sub>C to give CH<sub>3</sub> groups. Subsequent presence of chemisorbed H<sub>2</sub> yields CH<sub>4</sub>, while the lack of chemisorbed H<sub>2</sub> allows the CH<sub>3</sub> groups to link up to give long chains.

638. ———. Function of the Promoters in the Catalysts for the Fischer-Tropsch Synthesis. Trans.

Faraday Soc., vol. 42, 1946, pp. 580-585; Chem. Abs., vol. 41, 1947, p. 262.

Determinations were made on 5 catalysts to learn which of these should be the most effective catalyst for the Fischer-Tropsch synthesis. The 5 catalysts were: (1) Co; (2) Co-ThO<sub>2</sub> 100:18; (3) Co-kieselguhr 1:1; (4) Co-ThO<sub>2</sub>-kieselguhr 100:18:100; (5) Co-ThO<sub>2</sub>-kieselguhr 100:21:100. They were all prepared from solutions of the nitrates of Co and Th, with addition of kieselguhr, by precipitation with K<sub>2</sub>CO<sub>3</sub> and reduction by H<sub>2</sub> at 375°. Both the initial fast and the final slow rate of carbide formation by the reaction 2CO+2Co=Co<sub>3</sub>C+CO<sub>2</sub> was promoted most effectively by (2) followed by (4) and (5), the latter much more slowly than (4). ThO<sub>2</sub> and kieselguhr are found to be strong promoters for the reduction of Co<sub>3</sub>C by H<sub>2</sub>. Of all the catalysts used, with the exception of (1), (4) gave by far the slowest rate of reduction of the carbide and, thus, has both a relatively slow rate of carbide reduction and a relatively fast rate of carbide formation, confirming the previously expressed view about the mechanism of the Fischer-Tropsch reaction according to which the rate of formation of carbide by the reaction 2Co+H<sub>2</sub>+CO=Co<sub>3</sub>C+H<sub>2</sub>O must be faster than the reduction of the carbide to allow for the accumulation of surface carbide during the reaction, and the consequent exclusion of chemisorbed H<sub>2</sub> from the surface if oils are to be formed: (2) has a very high rate of carbide formation but is not a good Fischer-Tropsch catalyst because it shows too high a rate of carbide reduction; (5) is poor in 2 respects. Its rate of carbide formation is slow compared with the normal active Fischer-Tropsch catalyst, and its rate of carbide reduction is high.

639. ———. Mechanism of the Fischer-Tropsch Reaction. Trans. Faraday Soc., vol. 42, 1946, pp. 576-580; Chem. Abs., vol. 41, 1947, p. 262.

The theory of the Fischer-Tropsch reaction has been proposed in which hydrocarbon oils are synthesized from a suitable mixture of CO and H<sub>2</sub> over a Co catalyst when the Co in the catalyst surface is in the form of the carbide Co<sub>3</sub>C, and the Co in the uncombined form gives CH<sub>4</sub>, allows the water-gas-shift reaction to take place, and is active for the hydrogenation cracking of hydrocarbons. The formation of higher hydrocarbons must be examined in greater detail to see whether the results of the synthesis can be accounted for by the above mechanism. When synthesis gas (CO+2H<sub>2</sub>) is passed over the catalyst (100 Co+6 ThO<sub>2</sub>+12 MgO+200 kieselguhr) at 185°, it is found that the yield of liquid hydrocarbons and the amount of CO<sub>2</sub> formed, both expressed in gm. per N m.<sup>3</sup> of synthesis gas, change with change of synthesis-gas rate. The oil yield is a maximum for a rate of about 1 l. per gm. Co per hr. and falls off for higher and lower rates, and the amount of CO<sub>2</sub> formed is small for rates higher than the above but increases rapidly at smaller gas rates. At low gas rates oil synthesis occurs only on the front part of the catalyst bed where the Co of the catalyst is largely converted to carbide and there is little chemisorbed H<sub>2</sub>. The rest of the catalyst bed, where oil synthesis is not taking place actively, is relatively free from carbide and therefore available for the water-gas-shift reaction. Further, the small amount of CO<sub>2</sub> produced at the maximum gas rate for oil production shows that the formation of CO<sub>2</sub> and the oil-forming reaction do not occur simultaneously as 2CO+2H<sub>2</sub>=CO+—CH<sub>3</sub>, but the former is separate and occurs later. The oil-forming reaction must, therefore, be CO+2H<sub>2</sub>=H<sub>2</sub>O+—CH<sub>3</sub>, followed, when conditions permit, by the water-gas-shift reaction. Variation in the oil yield with the synthesis gas rate is also explained very simply on this basis. At a gas rate of 1 l. per gm. Co per hr. the entire catalyst is actively synthesizing oil. At higher gas rates the oil yield decreases as the contact

time of the gas with the catalyst diminishes, and the synthesis is not completed. At lower gas rates, the synthesis is completed on the first part of the catalyst bed and the oil formed there passes over the uncarbided second portion of the bed covered by chemisorbed H<sub>2</sub>, and is hydrogenated-cracked with formation of CH<sub>4</sub>.

640. ———. Chemistry of the Fischer-Tropsch Synthesis. Fuel, vol. 26, No. 5, 1947, pp. 119-123; Chem. Abs., vol. 42, 1948, p. 787.

Paper read before the 11th International Congress of Pure and Applied Chemistry. The best catalyst for the Fischer-Tropsch synthesis reaction is 100 Co : 5 ThO : 8 MgO : 200 kieselguhr, in which the ThO and the MgO play only a minor role, the Co and the kieselguhr being the active components. The kieselguhr has two functions both of which are important: To insure that the reduced Co is produced and maintained in an exceedingly finely divided form; and to establish and maintain the porosity of the individual catalyst granules. It is believed that the catalyst is not a mixture of these two constituents but rather a chemical combination of the two. The fact that these Co-kieselguhr preparations are much more difficult to reduce than Co-carbonate alone is a further indication of chemical interaction and, in particular, of silicate formation. The importance of the 2d function of kieselguhr is seen in connection with the removal of the synthesis products from the catalyst and with maintaining the catalyst surfaces in a receptive state. Active catalysts do not consist of bulk metallic Co with the normal lattice but rather with layers of Co atoms having an arrangement based on the structure of Co silicate, ordinary Co carbide thus playing no part in the reaction. When CO alone reacts with the reduced catalyst, the reaction is much faster than when it reacts with Co metal. In both cases the CO is first chemisorbed on a Co atom, and the O atom is removed by reaction with a second molecule of CO, leaving a chemisorbed O atom. In the case of bulk carbide very little CO can react in this way, and the rate is then determined by the rate of diffusion of the chemisorbed O atoms into the interior of the lattice to give Co carbide. In the case of the catalyst, on the other hand, nearly all the Co atoms are available in the surface for reaction with CO so that the rate of reaction is fast, and the final result is an array of chemisorbed C atoms. If CH<sub>4</sub> is added to the mixture of CO and H<sub>2</sub>, not only is the normal formation of CH<sub>4</sub> by the synthesis entirely suppressed, but some of the added CH<sub>4</sub> enters into the reaction and polymerizes with the CH<sub>3</sub> groups on the catalyst surface to give higher hydrocarbons. This effect has also been observed in synthesis in 2 stages; it is believed that this effect is due to formation of a polymerization-depolymerization equilibrium.

641. ———. Fischer-Tropsch Synthesis With Cobalt Catalysts. Jour. Soc. Chem. Ind., vol. 66, 1947, pp. 440-444; Chem. Abs., vol. 42, 1948, p. 3648.

Summary of more academic aspects of the research and development work carried out in Germany and elsewhere in recent years. The composition and method of preparation of the Co catalyst are described, and the influence of the activators ThO<sub>2</sub>, MnO, and MgO on the working of the catalyst is discussed. The importance of kieselguhr as a carrier is emphasized, and the 2 functions of maintaining the Co in a finely divided form after reduction and of preserving the porosity of the individual granules are examined. The reduction of the catalyst is considered to be the most crucial step in the entire process, and the 3 factors of temperature, time, and H<sub>2</sub> rates must be carefully observed. Deterioration of the catalyst during synthesis at both atmospheric and medium pressure appears to be mainly the result of wax formation

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on the catalyst granules, and the rate of deterioration can be closely correlated with the rate of deposition of such waxes on the catalyst. It has been concluded that ordinary Co carbide plays no part in the synthesis reaction: the Co atoms appear to be isolated and do not form part of a Co lattice. Reaction by way of chemisorbed C atoms, the so-called surface carbide, however, is thought to give an array of interacting CH<sub>3</sub> groups on the surface, and the composition of the products, which are obtained from this array, depends on the conditions surrounding the conversion. Some recent work has even tended to emphasize the idea of a polymerization-depolymerization equilibrium.

See abs. 1326, 1334, 1335, 1336.

642. CRANFORD, S. R., AND POLL, A. [Reduction of Catalysts With a Cobalt and Kieselguhr Base Utilized in the Fischer-Tropsch Synthesis.] Jour. chim. phys., vol. 47, 1950, pp. 253-257; Chem. Abs., vol. 44, 1950, p. 8086.

Catalysts having the composition Co:ThO<sub>2</sub>:MgO:kieselguhr in the ratio 100:6:12:200 were used. The most active catalyst was obtained by carrying out the reduction at 400° in pure dry H<sub>2</sub> at a flow rate of 6,000 vol./vol. of catalyst/hr. When H<sub>2</sub> saturated with H<sub>2</sub>O vapor at room temperature was used for reduction, the surface area of the reduced portion of the catalyst was slightly greater than that observed with dry H<sub>2</sub>, but the amount of reduction was appreciably less. The % reduction of Co oxide after treatment with dry H<sub>2</sub> under the above conditions was 29.8 at 300°, 53.2 at 350°, 71.2 at 400°, 81.3 at 450°, and 91.5 at 500°. A reduction temperature of 400° caused the least diminution of the surface area after vacuum treatment at 450° for 4 hr. A reduction in surface area from 229 m<sup>2</sup>/gm. of Co to 180 m<sup>2</sup>/gm. occurred when the catalyst was used in synthesis. Along with x-ray data, the diminution in surface area suggested that appreciable agglomeration of Co occurred during use of the catalyst. Catalysts were prepared in 5 different manners to investigate the role of the formation of a hydrosilicate on the reduction. Conditions favoring the formation of a hydrosilicate appreciably decreased the ease of reduction. A catalyst that was maintained at an elevated temperature under pressure in an autoclave during preparation could not be reduced with H<sub>2</sub> at 800°. The minimum amount of reduction in surface area occurred under conditions of catalyst preparation that did not favor formation of a hydrosilicate.

643. CRANFORD, S. R., AND RIDEAL, E. K. Mechanism of the Synthesis of Hydrocarbons From Water Gas. Jour. Chem. Soc., 1939, pp. 1604-1614; British Chem. Abs., 1940, B, p. 8; Chem. Abs., vol. 34, 1940, p. 1464.

Experiments on the rates of formation and reduction of Co<sub>3</sub>C on Co-Th-kieselguhr catalysts under various conditions indicate that the first step in the Fischer-Tropsch synthesis of hydrocarbons from CO and H<sub>2</sub> is the reaction of these gases with the catalyst to give Co carbide. As indicated by the *o-p*-H<sub>2</sub> conversion, when carbide is reduced only CH<sub>4</sub> is formed and no higher hydrocarbons. Reduction by H<sub>2</sub> leads to formation of oils. Curves are given for the rates of the reactions between Co and CO, between Co<sub>3</sub>C and H<sub>2</sub>, on the Fischer catalyst, for the energies of activation of the reaction Co<sub>3</sub>C+2H<sub>2</sub>, and for the total reaction CO+2H<sub>2</sub>. It is concluded that, in order to obtain oils, the conditions of the synthesis have to be adjusted so that only very few chemisorbed H<sub>2</sub> atoms are present on the catalyst surface.

644. CRENTZ, W. L., DOHERTY, J. D., AND DONATH, E. E. Coal Preparation for Synthetic Liquid Fuels. Min. Eng., Trans. Am. Inst. Min. and Met. Eng., vol. 187, 1950, pp. 507-510.

Principal washing problems in preparing coal for the synthetic fuel industry may be stated as: (1) Ash re-



moral for the Bergius process; and (2) S removal for the Fischer-Tropsch process. A study is made of the effect of ash on oil losses during the elimination of the nonliquefiable portions of the coal in the hydrogenation process. The oil loss increases with ash content of the coal and results in increased consumption of coal, H<sub>2</sub>, and power. Quantitatively, it is estimated that the oil loss due to ash amounts to about 9 lb. of oil for each % of ash in 1 ton of the hydrogenated coal. Cost comparison is made of the economic advantages resulting from the use of 2.3% ash coal and a 6% ash coal in a 30,000 bbl./day hydrogenation plant. In the Fischer-Tropsch process, the quantity of ash in the raw-coal feed is not as critical as in the Bergius process. The problem here is the amount of S that the synthesis gas contains. The economic advantage, however, lies with the cleaning of the coal used to make synthesis gas to a low S content if the S can be removed by mechanical cleaning. It is estimated that it costs \$1.15/ton of gasified coal to remove S from synthesis gas when the coal contains 3% S. Increase in the S content of the coal from 3 to 5% would impose an additional cost of \$0.37/ton.

CHITTENDEN, E. D. See abs. 36, 3748.

645. CROFT, C. M. Installation of Tower Gas Purifiers. Inst. Gas Eng., Commun. and Repts., vol. 212, 1930, 18 pp.; Chem. Abs., vol. 33, 1930, p. 6563.

Thyssen-Lenze tower gas purifiers, the first of their kind in England, as installed at the Wandsworth Works, are described. The installation, capacity 10,000,000 cu. ft./day, consists of 6 towers, together with a stocking tower and stocking frame. The purifiers have worked equally well from 1/4 capacity to 3/4% overload. To date, the spent oxide has contained 44% pure S. Costs are about 1/2 those of the original purifiers.

645a. CROMEANS, J. S. Hydrogenation and Hydrogenolysis. Ind. Eng. Chem., vol. 44, No. 9, 1952, pp. 2025-2036.

Review of the literature and patents occurring in 1951 on the Fischer-Tropsch process and other processes involving hydrogenation. Bibliography of 323 refs.

CROSS, A. C. See abs. 3303.

CROWELL, J. H. See abs. 2097, 3090.

646. CROWELL, J. H., and BENSON, H. E. Direct Evaporative Cooling in the Synthesis of Liquid Hydrocarbons From Hydrogen and Carbon Monoxide. Am. Chem. Soc., 111th Meeting Abs., 1947, p. 14 I.

Brief summaries of the German method for heat removal from the Fischer-Tropsch converter and of such developmental processes as the hot-gas recycle, the oil slurry, and the fixed-bed oil-recycle processes. The early laboratory investigations by the Bureau of Mines upon the principle of direct evaporative cooling of the fixed bed are also described. In this method oil is allowed to trickle down over the catalyst bed, and the vaporization of this oil removes the heat of the reaction. The catalyst bed in the small unit was 3 in. diameter and 12 in. length. Mechanical operation was very smooth and temperature control was quite satisfactory. Construction and operation of a larger unit of the same diameter but 8 ft. long is described in detail. Provision was made for oil injection at various points in the column along with other improvements in design. The productivity is currently about 1 gal. of primary product/day and tabulated data are given for products, yields, and operating information for space velocities varying from 100 to 300. Future plans for study and pilot-plant development are discussed.

647. CROWELL, J. H., BENSON, H. E., FELD, J. H., and STROCH, H. H. Fischer-Tropsch Pilot-Plant Studies of Oil-Circulation Processes at Bureau of Mines. Am. Chem. Soc., 117th Meeting Abs., March-April 1950, p. 5-J.

Summary of Fischer-Tropsch process development is given in which the essential features of the German fixed-bed system, the hot-gas recycle and oil-circulation processes, and the oil-slurry and fluidized-bed system are briefly described. Most of the pilot-plant experimentation at the Bureau of Mines has been directed toward the development of the oil-circulation process since a simple converter design could be used and precise operating control could be attained in such a system. Several moderately successful experiments were performed that employed a cooling-oil circulation through a fixed catalyst bed. However, shutdowns were necessary after 3 or 4 months of synthesis because the catalyst particles became cemented together and an excessive pressure drop developed across the catalyst bed. This problem of catalyst cementing was circumvented by employing a moving-bed catalyst in which the lifting action of the circulating oil was used to expand the catalyst bed and keep the particles in motion. Details of induction and synthesis operations, operating data, analyses of gas and liquid streams, tables of calculated yields, and a typical product distribution are given for various experiments. Calculations are made for a 2-stage process, with interstage scrubbing of CO<sub>2</sub>, showing the C, C<sub>2</sub>, and C<sub>3</sub> yields, which could be expected at a 91% overall synthesis-gas conversion.

648. ———. Fischer-Tropsch Oil-Circulation Processes. Ind. Eng. Chem., vol. 42, No. 11, 1950, pp. 2376-2384.

See abs. 647.

CRUMLEY, P. See abs. 1326a.

649. CRUTCHFIELD, J. W., and PIURETT, H. T. Engineering Developments in Southwest Texas. Petrol. Eng., vol. 18, No. 1, 1946, pp. 208, 210; Chem. Abs., vol. 41, 1947, p. 261.

Brief account of the Carthage Hydrocol, Inc., development at Brownsville utilizing a modified Fischer-Tropsch process. The plant will process 64,000,000 cu. ft. of dry gas/day, yielding 3.84 and 0.78 gal. respectively of gasoline and Diesel fuel/1,000 cu. ft. of gas. Development of the process is traced with special reference to the production of cheap O<sub>2</sub> and the conversion of CH<sub>4</sub> into CO and H<sub>2</sub> by the direct reaction of CH<sub>4</sub> and O<sub>2</sub>.

CRUYDER, D. S. See abs. 1103.

CRUYDER, D. S., and FROLICH, P. K. Catalyst for the Formation of Alcohols From Carbon Monoxide and Hydrogen. IV. Decomposition and Synthesis of Methanol by Catalysts Composed of Zinc and Chromium Oxides. See abs. 1101.

650. CUELLAR, F. T. Organic Bases and Salts for the Purification of Gas. Ion, vol. 5, 1945, pp. 755-760; Chem. Abs., vol. 41, 1947, p. 2863.

Review of substances used in the removal of undesirable constituents of gases used in the synthesis of NH<sub>3</sub>, the Fischer synthesis, and hydrogenation. 12 refs.

651. CUMMINGS, A. D. Oil From Coal: How Germany Synthesized Petrol for War. Discovery, vol. 9, February 1948, pp. 54-57; Fuel Abs., No. 3062, 1948.

Two processes, hydrogenation and the Fischer-Tropsch synthesis, are outlined. The Pintsch-Hillebrand, Wintershall-Schmalfeldt, and Winkler systems for utilizing brown coal in the synthesis are described, and the compositions of the gas mixtures from the 3 are compared.

652. CURIE, P. [Magnetic Properties of Materials at Various Temperatures.] Ann. chim. phys., Ser. 7, vol. 5, 1895, pp. 289-405.

653. CZERMAK, A. [Utilization by Processing of Low-Grade Coals As Well As Liquefaction of Coals.] Montan. Rundschau, vol. 19, 1927, pp. 283-290, 309-316, 337-344, and 371-375; Chem. Abs., vol. 21, 1927, p. 4047.

Outline of the chemical properties of C and several series of hydrocarbons is followed by a discussion of the methods for utilizing brown coals, lump coal, and lignites. Effects upon the coal, its byproducts, and heating values are given of the following: Improvements in byproduct oven design; drying of the coals by applying steam under pressure; the Bertinierung process; the carburization or Delkeskamp method; and the swelling processes. Descriptions of these processes, sectional diagrams of a Rolle-Oven installation, several

654. DAHM, ———. [Influence of the Iron Content of Kieselguhr on the Properties of Catalysts for the Hydrocarbon Synthesis.] FIAT Reel K29, 1939, frames 6,945-6,948; TOM Reel 296; PB 70,218.

Object of the work was to determine whether a favorable influence on the course of the synthesis with regard to an important reduction in the formation of CH<sub>4</sub> can be obtained by extracting the Fe from the kieselguhr used for catalysts. The answer is negative. 2 graphs.

654a. DALE, B., LEACH, J. R., BECKETT, C. W., and JOHNSTON, H. L. Survey of the Scientific Literature on the Fischer-Tropsch Process. Ohio State Univ. Research Foundation, Tech. Rept. Project RF-319, 1950, 78 pp.

Review with 474 refs.

655. DAL PRATO, L. [Transformation of Heavy Mineral Oils Into Benzine.] Rass. min. met. chim., vol. 61, 1924, pp. 118-122, 153-158; vol. 62, 1925, pp. 12-14; Chem. Abs., vol. 19, 1925, p. 1492.

General review of present developments in the conversion of oils to benzine by cracking, by heating under pressure with H<sub>2</sub>, and by catalytic decomposition and of attempts to synthesize hydrocarbons from H<sub>2</sub> and CO. Describes a new process developed by Dal Prato, consisting of the catalytic decomposition of complex molecules of the heavy hydrocarbons to benzine and gases and the catalytic synthesis of these gases to benzine. Process does not include hydrogenation.

656. ———. [Synthetic Petroleum.] Rass. min. met. chim., vol. 62, 1925, pp. 64-67, 91-93, 113-116; Chem. Abs., vol. 19, 1925, p. 2873.

Describes processes for synthesizing hydrocarbon fuels from C, H<sub>2</sub>, and simple gaseous compounds of these elements, including industrial preparation of illuminating gas, water gas, CH<sub>4</sub>, and H<sub>2</sub>; polymerization of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub>; hydrogenation of C<sub>2</sub>H<sub>4</sub> and C of Sabatier, Berthelot, Fischer, and Bergius and their transformation to liquid hydrocarbons; oxidation of Cand of CH<sub>4</sub> to liquid fuels by the Fischer process; and synthesis of petroleum by the Olivier and Burgeois process.

657. DAMKÖHLER, G. [Excess Temperature in Catalyst Grains.] Ztschr. physik. Chem., vol. 193, 1943, pp. 16-28; Chem. Abs., vol. 39, 1945, p. 2689.

The maximum excess temperature,  $\theta_{max}$ , in a stationary catalyst grain during reaction is independent of the chemical reaction velocity, as well as the radius of the grain and is determined solely by the heat of reaction  $Q$ , the internal diffusion coefficient  $D_1$ , the internal thermal conductivity  $\lambda$ , and the external concentration  $c$  of the reactants. The following equation was derived:

$$\theta_{max} \approx QD_1(c_1 - c_2)/v_1\lambda \text{ where } c_1$$

is the equilibrium concentration of reactants and  $v_1$  is the stoichiometric coefficient of constituent  $i$ . Calculated  $\theta_{max}$  for SO<sub>2</sub> oxidation was 0.42°, for NH<sub>3</sub> synthesis 0.20° at 200 atm. and 0.57° at 1,000 atm., for MeOH synthesis 1.0°, for butane synthesis from CO and H<sub>2</sub> 3.0°. This behavior of an individual catalyst grain is quite different from that of a converter

tables of data obtained using different kinds of coals, and manufacture and uses of producer gas and Grudek are included. The distribution and economics of the petroleum industries are discussed from the national and world standpoints. The experiments of Bergius and of Fischer in making liquid fuels from coal are reviewed, and compared, and the importance of these processes to countries that do not possess petroleum fields is emphasized. Gives number of refs. to recent articles on liquefaction.

D where chemical reaction velocity and dimensions of the reaction vessel are of importance.

658. DAMM, P. [Synthetic Alcohols—Manufacture of Synthetic Ethyl and Methyl Alcohol by the Mining Company of Bethune.] Mon. produits chim., vol. 11, No. 114, pp. 1-5; Chem. Zentralbl., 1928, II, p. 2208; Chem. Abs., vol. 23, 1929, p. 4668.

Report on synthetic manufacture of EtOH and MeOH from coke-oven gases, consisting chiefly of H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, CO, and N<sub>2</sub>. H<sub>2</sub> is separated by liquefaction of the rest of the gases. C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, and CO can be separated by the same method. C<sub>2</sub>H<sub>4</sub> is converted into EtOH by means of H<sub>2</sub>SO<sub>4</sub>. A suitable mixture of H<sub>2</sub>, CO, and N<sub>2</sub> serves for the synthesis of MeOH according to the equation: CO + 2 H<sub>2</sub> = CH<sub>3</sub>OH. For this reaction a catalyst is used whose composition is kept secret. NH<sub>3</sub> is synthesized from the remaining mixture of H<sub>2</sub> and N<sub>2</sub>. It is still more advantageous to make MeOH from water gas. MeOH should have a promising future because it is an excellent motor fuel.

659. DANĂILĂ, N., and BOLTUȘ-GORUNEANU, M. [Preparation of the Higher Fatty Acids From Mineral Oil and Paraffin by Oxidation With Air at Ordinary and at High Pressures With and Without Catalysts.] Bul. Chim. Soc. Română Științe, vol. 31, 1929, pp. 133-200; British Chem. Abs., 1932, B, p. 790; Chem. Abs., vol. 24, 1930, p. 2232.

Detailed review of the literature from 1855. At ordinary pressure the oxidation of paraffin in the presence of Cu gave solid fatty acids, while mineral oil yielded only semisolid fatty acids resembling humic acids. Only the acids from paraffin can have practical application. Oxidation at ordinary temperature produces colored, malodorous byproducts and hydroxy acids, which diminish the value of the Na soaps. Better yields, 53%, were obtained by repeating the oxidation of the paraffin at increased pressure in the Bergius bomb and still better, 75%, by threefold oxidation. The fatty acids are colorless and odorless, and their molecular weights are not far from that of stearic acid. The Na salts are solids that foam freely. They could be employed in soap making. Na salts of acids made from mineral oils are liquids that foam readily. They could be employed as liquid soaps. A preliminary treatment of the mineral oils for removing the unsaturated aromatic and naphthene hydrocarbons increases the yields of fatty acids.

660. DANCKWERTS, P. V. Absorption by Simultaneous Diffusion and Chemical Reaction. Trans. Faraday Soc., vol. 46, 1950, pp. 300-304; Chem. Abs., vol. 44, 1950, p. 8706.

Equations are derived for the rate of absorption and the concentration when a solute of limited solubility diffuses into a semi-infinite medium with which it undergoes a 1st-order reaction. Consideration is given to the case where the medium is a mixture only 1 component of which reacts. Examples are the absorption of a gas into a liquid or solid, the solution of a solid into a supernatant liquid, or the absorption of 1 solid or liquid material into another.

661. DANNEFELSER, W. [Knock Measurements on Synthetic Gasoline.] Oel u. Kohle Erdoel Teer, vol.