

thetic fuels from coal is reviewed, and the present program is outlined. The greater progress made in the hydrogenation of CO, as compared with that in hydrogenation of coal, is due to the inherently greater simplicity of the chemistry involved in the mechanisms concerning CO. In addition to the dearth of laboratory and experimental-plant research on coal hydrogenation, the meager knowledge of the chemical constitution of coal and of the mechanism of its pyrolysis and hydrogenolysis has greatly retarded the development of new processes. For this reason, emphasis must be placed on the acquisition of basic information on the chemistry and physics of coal. In synthesizing liquid fuels from coal by way of synthesis gas, about 60-70% of the cost of the liquid fuel product lies in the synthesis gas itself. Therefore, a very efficient conversion of this mixture of H₂ and CO is necessary if the process is to be industrially successful. 2 methods to accomplish this are being studied: The internally cooled, fixed-catalyst-bed process, in which the exothermic heat is removed efficiently and rapidly by the circulation of a relatively nonvolatile oil through the bed of granular catalyst; and the oil-catalyst-slurry process, in which a powdered catalyst is suspended in an oil that is nonvolatile under operating conditions and the synthesis gas is bubbled through this suspension. The 2d method is less efficient than the 1st in that the conversion of CO is only about 25-50% of that obtained in the 1st method. It does, however, have the advantage of the possible continuous removal of partly spent catalyst and the continuous introduction of regenerated or fresh catalyst. As regards the direct hydrogenation of coal, a basically new approach and a radical departure from the conventional Bergius process is under investigation. It is based on the rapid conversion of coal to distillable oil, gas, and coke at moderate pressure and relatively high temperatures. 2 times as much coal as is required for hydrogenation is passed through the reactor; about 1/2 of this is converted to oil and gas and the remainder to coke which is burned for steam and power production. This makes possible the appearance in the oil and gas of the H₂ from that half of the coal feed converted to coke. It has been found possible to replace the H₂ by water gas under proper operating conditions. Since H₂ constitutes about 50% of the total cost of the liquid fuels, this is an important consideration. Use of byproduct hydrocarbon gases, which, when reacted with steam, yield a mixture of CO₂ and H₂, also save in the cost of H₂.

3291. Fischer-Tropsch and Related Processes for Synthesis of Hydrocarbons by Hydrogenation of Carbon Monoxide. Advances in Catalysis, Academic Press, Inc., New York, 1948, vol. I, pp. 115-156.

Review. The following points are discussed: Development of the Ruhrchemie process and modifications thereof, such as Lurgi, L. G. Farbenindustrie, A.-G., fluidized catalyst; related processes, such as Synol, Oxo, and isosynthesis; carbide and elemental C formation; kinetics and reaction mechanisms. 91 refs.

3292. Review of Development of Processes for Synthesis of Liquid Fuels by Hydrogenation of Carbon Monoxide. Chem. Eng. Progress, vol. 44, No. 6, 1948, pp. 469-480; Chem. Abs., vol. 42, 1948, p. 5200.

Brief review of the early work of Fischer and his associates is followed by a more detailed discussion of process development work in Germany and the United States since about 1938. The salient features of all processes are collected in a single table, so as to facilitate comparisons of operating temperatures, pressures, space-time yields, product distribution, and steel requirements. Also describes related processes, such as the Synol, Oxo, and isoparaffin syntheses. Some discussion of the mechanism of the synthesis process and of the problem of C deposition on Fe catalysts.

3293. Liquid Fuels From Coal and Oil Shales. Advances Chem. Ser. No. 5, 1951, pp. 138-150; Chem. Abs., vol. 45, 1951, p. 10,558.

Desirability of long-range development work on synthetic liquid fuel processes is discussed. The basic chemical and engineering problems involved in coal gasification, coal hydrogenation, hydrogenation of CO, retorting of oil shale, and refining of oil shale are presented. Brief mention is made of shale oil are experiments in hydrocarbonization of coal in a fluidized bed at H₂ pressures of 1,000 p. s. i. or less. 37 refs.

3293a. [Liquid Fuels From Coal and Oil Shale.] Riv. combustibili, vol. 6, 1952, pp. 139-163; Jour. Inst. Petrol., vol. 38, 1952, p. 397 A.

See abs. 42a, 43, 50, 98, 647, 648, 1232, 1370, 2035, 2102, 2103a, 3090, 3654, 3656.

3294. Storch, H. H., and Golden, P. L. Preparation of Pure Methane From Natural Gas. Jour. Am. Chem. Soc., vol. 54, 1932, p. 4662; Chem. Abs., vol. 27, 1933, p. 539.

Higher hydrocarbons are removed from natural gas by passing it through a layer of active coconut charcoal.

3295. Storch, H. H., and Pinkel, I. I. Preparation of an Active Cobalt-Copper Catalyst for the Water-Gas Shift Reaction. Ind. Eng. Chem., vol. 29, 1937, p. 715; Chem. Abs., vol. 31, 1937, p. 5977.

If a mixture of CoCO₃ and 5-25% of CuO is heated rapidly (in about 3 min.) from room temperature to 900°-1,100° C., a sintered, pumicelike mass of granules is obtained, which has excellent mechanical properties and is a very active catalyst when properly reduced and subsequently protected from S poisoning. Slower heating of the mixture results in a powder of inferior quality. A mixture of water gas with 4 vol. of steam was passed through this catalyst at 310° C. for more than 100 hr. without impairing the activity. The original water gas contained about 68% H₂, 23% CO, and small amounts of CO₂, N₂, CH₄, and O₂. The average analysis of the gas after the catalytic treatment was 73.8% H₂, 0.3% CO, 18.7% CO₂, with the remainder N₂ and CH₄. The activity of the catalyst is destroyed rapidly by contact with S compounds but easily can be regenerated to its original properties by heating to 900° C. in a stream of air.

3296. Storch, H. H., Golumbic, N., and Anderson, R. B. The Fischer-Tropsch and Related Syntheses. John Wiley & Sons, New York, 1951, 610 pp.

Much current interest has been aroused by the Fischer-Tropsch process—a process that will undoubtedly benefit our fuel economy when its technology becomes better known and more profitable. Its possibilities are being explored in several directions at the present time; ultimately this versatile and flexible process may play a major role in the utilization of our fuel resources. Written primarily for chemists and chemical engineers engaged in the Fischer-Tropsch or similar process development, this book, in the main, is concerned with a critical review of the development of this and related syntheses. The Fischer-Tropsch process—one of the most-recent advances in the scientific and industrial development of CO reactions—synthesizes liquid aliphatic hydrocarbons, alcohols, fatty acids, ketones and aldehydes by hydrogenation of CO. The basic chemistry, industrial operations, and the result of catalyst testing and pilot plant developments by industrial laboratories and by the Bureau of Mines are presented together with a discussion of theoretical and applied contact catalysis, synthesis mechanism, kinetics, and thermodynamics.

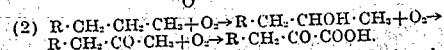
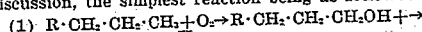
3297. Storch, H. H., Anderson, R. B., Hofer, L. J. E., Hawk, C. O., Anderson, H. C., and Golumbic, N. Synthetic Liquid Fuels From Hydrogenation of

Carbon Monoxide. Bureau of Mines Tech. Paper 709, 1948, 213 pp.

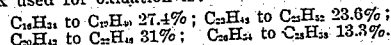
This paper contains a review of the literature up to October 1946, a report of Bureau of Mines research on the effect of preparation, reduction, and induction procedures on the activity of the catalysts and a correlation of the physical properties of the catalysts with their activity. The paper also includes data on the X-ray diffraction patterns, the magnetic susceptibility, the surface area, and the porosity of the catalysts.

3298. Srossel, E. Oxidation of Paraffins. Oil Gas Jour., vol. 44, 1945, No. 11, pp. 130, 132, 134, 137, 139; No. 15, pp. 145, 147, 148, 151; No. 17, pp. 69, 70, 73, 74, 77.

Major steps in the oxidation of paraffin waxes to form fatty acids and other oxygenated products are presented together with the various theories of the sequence of steps in the oxidation process. Also discussed are the possibilities of synthetic fatty acids produced by oxidation of paraffin in the light of the cheap raw materials made available in the slack wax from the Fischer-Tropsch synthesis. Consideration also is given to the closely related products and intermediates of the paraffin oxidation reaction, for example, alcohols, aldehydes, ketones, and wax esters. The mechanism of the oxidation is still a matter of discussion, the simplest reaction being as follows:



It is not as simple as this, however, since H₂O, formic acid, and peroxides are always formed. One theory postulates that our C-H bond is split and unsaturated compounds are formed, which subsequently oxidize; another proposes the free radical mechanism whereby the attack takes place through rupture of a C-C bond; by the peroxidation mechanism, peroxides are always formed at the start and reach a maximum after 2-3 hr., after which they decrease rapidly and acid formation takes place; by the hydroxylation theory, alcohols are formed as the 1st step in the sequence: Hydrocarbon-alcohol-glycol-aldehyde-acid-carbon dioxide, the process repeating itself until the final degradation products are CO₂ and H₂O. Below 100° C., oxidation proceeds slowly, but, by preheating the hydrocarbons with alkali manganates to 100°-200° for several hr., oxidation proceeds well at 80°-100°. The longer the straight chain of C atoms contained in organic molecules, the less difficulty is encountered in their oxidation. Oxidation also is preceded by an induction period, after which the reaction is more rapid. The use of catalysts shortens the oxidation period by eliminating the induction period, destroying anti-oxygens or inhibitors present in the original material, and producing pro-oxidants, which direct the course of the oxidation. Catalytic material from a few thousandths up to 3% by weight of the initial material is generally used. Suitable catalysts are carboxylic acid salts, especially those of higher fatty acids, and oxides of the metals of groups 5 and 6. There is an optimum temperature range, which varies with the materials used and the results desired. For maximum yields of alcohols or high-molecular weight fatty acids the oxidation temperature is kept 110°-140° at a pressure of 60-150 p. s. i. A typical analysis of a Fischer-Tropsch slack wax used for oxidation is:



Bibliography of 145 refs.

3299. Strada, M. [Catalysts in the Synthesis of Aliphatic Alcohols: Their Behavior and the Relation Between Their Composition and Activity.] Giorn. chim. ind. applicata, vol. 14, 1932, pp. 601-607; British Chem. Abs., 1933, B, p. 259; Chem. Abs., vol. 27, 1933, p. 2131.

It has already been shown in the previous papers that K salts of aliphatic acids catalyze the synthesis of alcohols from CO and H₂. The results make it seem probable that the presence of the K salt of the particular alcohol desired would accelerate the formation of this alcohol. As catalysts, HCO₂K, AcOK, EtCO₂K, PrCO₂K, and BuCO₂K were used. HCO₂K and AcOK have the highest catalytic powers. Analysis of the catalyst after it has been in use for some time shows a composition tending to become the same regardless of which salt was used to start. The catalytic action is determined by the % of K₂O present rather than its form.

3300. [Influence of the Catalyst Used on the Purity of the Methyl Alcohol Produced Synthetically From Water Gas.] Giorn. chim. ind. applicata, vol. 15, 1933, pp. 168-176; Chem. Zentralbl., 1933, II, p. 278; Chem. Abs., vol. 27, 1933, p. 4632.

Systematic study of the action of various catalysts, which have been suggested or patented for the preparation of MeOH, including Zn⁽⁰⁾ obtained by various chemical means, ZnO and Cr₂O₃ in various proportions, ZnO-Al₂O₃, ZnO-MgO, ZnO-MnO, ZnO-Cr₂O₃-Fe₂O₃, and smithsonite from various sources. The smithsonites give the best results, the MeOH being more nearly pure; higher acids, aldehydes, and ketones are present in minute amounts, no higher alcohols are present, and the amount of hydrocarbon formed is low. Smithsonites also retain their activity much better than the artificially prepared catalysts examined.

3301. [Fatty Acids Formed Along With the Aliphatic Alcohols in Syntheses Under Pressure From Carbon Monoxide and Hydrogen.] Giorn. chim. ind. applicata, vol. 16, 1934, pp. 62-70; British Chem. Abs., 1934, B, p. 616; Chem. Abs., vol. 28, 1934, p. 5042.

In the acid portion of the product formed during the synthesis of alcohols from CO and H₂ under pressure, the following were identified: Normal acids, from formic to heptylic; isobutyric, isovaleric, isocaproic and isoheptylic; several acids with a side chain at the α-C (methylthylacetic, methylpropylacetic, and methylbutylacetic acids). The molecular weight of the high-boiling fraction indicates that acids containing 14-16 C atoms are present. The fact that most of the acids formed correspond to the alcohol also formed in this reaction tends to confirm the theory that the higher alcohols are derived by the reduction of the corresponding acid, that is, EtCO₂H + 2H₂ → EtCHOH + H₂O.

See abs. 2398, 2399, 2400.

STRAUSSER, W. A. See abs. 3182.

3302. STRAUSSER, R. [Fatty Acids by Oxidation of Hydrocarbons.] Fette u. Seifen, No. 10, 1936, p. 200; Petrol. Refiner, vol. 24, No. 2, 1945, pp. 73-76, 117-120.

Review of processes that lend themselves to commercial operation for the production of synthetic fatty acids derived from liquid or solid hydrocarbon material. 30 refs.

3303. STREVENIS, J. L., and Cross, A. C. Motor Spirit From Coal. Nature, vol. 141, 1938, pp. 812-814, 1058-1059; Chem. Abs., vol. 33, 1939, p. 3110.

Reviews hydrogenation, coal-oil distillation, and synthesis methods of production.

3304. STRICKLAND-CONSTABLE, R. F. Synthesis of Methane From Carbon Monoxide and Hydrogen on a Nickel Catalyst. Study of the Mechanism of Reaction. Gas Research Board Commun. 46; Gas

World, vol. 130, 1949, pp. 629-631; Chem. Abs., vol. 43, 1949, p. 7666.

It has been shown that a catalyst known as J14 made from a mixture of 3 parts hydrated Al(NO₃)₃ and 1 part hydrated Ni(NO₃)₂ on china clay is much better than a pure Ni catalyst for the synthesis of CH₄. In either case, the catalyst is precipitated by Na₂CO₃ and reduced in H₂. Reduction starts at 350° and is completed at 450°. If, after such a treatment, a synthesis reaction is carried out at 250° with an H₂:CO ratio of 3:1, it is found that equal volumes of H₂O and CH₄ are not produced in accordance with the equation 3H₂+CO→CH₄+H₂O, but that no water vapor is present in the gas phase, it being retained on the Al oxide part of the catalyst and not by the Ni. It is not known whether this retention of H₂O by the Al₂O₃ affects the synthesis reaction or not, but it is possible that this sorption of H₂O forms an integral part of the main synthesis reactions, and this may partly account for the great activity of the Al-containing catalyst. The general features of the synthesis reaction are interpreted.

3305. STRIMBECK, G. R. Use of Oxygen in Production of Synthesis Gas. Chem. and Eng. News, vol. 28, 1950, p. 1922.

Paper presented at the chemical conference of the American Gas Association. Operation of a Bureau of Mines pilot plant in Morgantown, W. Va., is described in which fluidized, 200-mesh coal had been gasified at efficiencies of up to 88% of the C converted. The process was run continuously on strongly coking coal at feed rates of 200-450 lb. of coal per hr. at temperatures of about 240°, 1,800°, and 3,000° F. The O₂ consumption was lowest in the high-temperature runs, requiring only about 170 cu. ft. per 1,000 cu. ft. of CO and H₂ produced. It is believed that this is the lowest O₂ consumption ever reported for a continuous synthesis-gas process. Coal consumption was reported as lowest in the hottest runs also, being only about 34 lb. per 1,000 cu. ft. of product, but steam consumption at 51 lb. per 1,000 cu. ft. was more than 2.5 times that for the lowest temperature and the % of C gasified was down to 83%. The process is thought to be adaptable to commercial production of synthesis gas, particularly since additional work indicated that the ratio H₂:CO could be adjusted within limits, and the type of coal is not critical to the performance of the process, thus permitting purchase of fuel on heat content considerations alone.

3305a. STRIMBECK, G. R., CORDNER, J. B., TAYLOR, H. G., PLANTS, K. D., AND SCHMIDT, L. D. Pressure Technique Lowers Cost for Synthesis Gases. Chem. Eng. News, vol. 30, 1952, p. 2392.

In a paper read at the American Gas Association meeting in May 1952, a report was made of the progress in the development, at the Bureau of Mines experimental plant, Morgantown, W. Va., of the direct coal gasification process. The plant is designed to gasify coal dust entrained in O₂ and steam at pressures up to 450 p. s. i. g. Test runs on pulverized Sewickley-bed coal at pressures of 100, 250 and 300 p. s. i. g. resulted in surprisingly large throughputs. Material requirements have been low per 1,000 ft.³ of CO and H₂ produced. At 300 p. s. i. g. gasifier pressure, over 500 lb. of coal per hr. per ft.³ of gasifier volume have been gasified. The material requirements at these throughputs were about 340 ft.³ O₂ and 35 lb. of coal per 1,000 ft.³ of CO and H₂, and with comparatively small heat losses per lb. of fuel. The process promises an excellent source of synthesis gas. Generation of the gas under pressure greatly lowers its cost by cutting the gas volumes to be compressed by 3/4 as only the O₂ needs to be compressed.

3306. STRIMBECK, G. R., HOLDEN, J. H., ROCKENBACK, L. P., CORDNER, J. B., AND SCHMIDT, L. D. Pilot-Plant Gasification of Pulverized Coal With Oxygen and Highly Superheated Steam. Bureau of Mines Rept. of Investigations 4733, 1950, 41 pp.; Bib. of Tech. Repts., vol. 15, 1951, p. 43; PB 101,553; Proc. Am. Gas Assoc., 1950, pp. 501-563.

Pilot-plant data are reported for 31 runs on the gasification of 90% through 200-mesh of a strongly coking Sewickley-bed coal with O₂ and with superheated steam in 3 temperature ranges 2,700°-3,400° F., 1,600°-2,000° F., and 230°-250° F. at feed rates of 200-450 lb. per hr. Average requirements per 1,000 std. cu. ft. of CO+H₂ produced are:

Steam temperature, °F.	Coal, lb.	O ₂ , std. cu. ft.	Steam, lb.
2,904	33.3	171	81.1
1,899	37.3	326	42.5
238	42.3	394	29.1

In general, the pilot plant performed very well. Continuous operation was possible, the runs being terminated voluntarily. The performance data indicate that the process could furnish low-cost synthesis gas on a commercial scale. The % gasification of the coal was very satisfactory. Average % C gasified was 88.9, 89.9, and 85.2 in the high-, medium-, and low-temperature steam runs, respectively. The O₂ requirement per 1,000 std. cu. ft. of CO+H₂ produced in the high-temperature steam runs was lower than for any other continuous process known. Correlations are presented on steam decomposition, O₂ required per 1,000 cu. ft. of CO+H₂ in the make gas, % CO₂ and H₂:CO ratio in the make gas. Refractory materials suitable for use in superheating steam to the range of 2,700°-3,400° F. have been found to be available at a reasonable cost. Apparatus is described with the aid of flow diagrams.

STRONG, H. W. See abs. 2448.

3307. STUART, A. T. Manufacture of Industrial and Domestic Gases by Means of Electricity (Complete Gasification of Coal With Oxygen). Am. Gas Jour., vol. 147, 1937, No. 1, pp. 19-22; Gas World, vol. 107, 1937, pp. 8-10; Canadian Chem. and Met., vol. 21, 1937, pp. 283-285; Gas Jour., vol. 219, 1937, pp. 343-344; Chem. Abs., vol. 31, 1937, p. 6442.

Gas of normal CO content and having the present standards of B. t. u. value, specific gravity, and composition, without any complex secondary processing, can be made by utilizing electrolytic O₂ and H₂ in place of air. A plant is described.

3308. STUHLFARNER, —. [Catalytic Cracking of Hydrocarbons.] FIAT Reel K-23, frames 6232-6259, Aug. 26, 1940, PB 70,135-s; TOM Reel 295.

It is desired to crack Diesel oils from the Fischer-Tropsch synthesis consisting of predominantly unbranched paraffins with 11-18 C atoms into hydrocarbons with 3-5 C atoms by polymerization by which antiknock gasoline can be obtained. The production of CH₄ and C hydrocarbons is to be avoided. In the apparatus described, natural and synthetic Al hydrosilicates were tested as catalysts and compared. Best results were obtained with those of Al₂O₃-4 SiO₂ composition. For the production of large amounts of unsaturated hydrocarbons, the catalysts must contain dehydrogenating additions such as Cr and Ba oxides. 1 diagram, 12 tables.

STURKEY, L. See abs. 1390.

SUCKSMITH, W. See abs. 635, 2694, 2695.

3309. SULLIVAN, F. W. Fuel-Synthesis Byproducts As Source of Chemicals. Chem. Eng. Progress, vol. 43, No. 12, 1947, pp. 13-17; British Abs., 1948, B, I, p. 283.

Impact that the synthetic chemical development by way of the Hydrocol process will have upon organic chemical production is presented, and the estimated production from a probable 10 Hydrocol plants is compared with U. S. production. The fact is that the total weight of the chemicals from Hydrocol operation on this scale is more than 3/4 the weight of the present production of these chemicals. Furthermore, the total volume of products from 10 plants would be considerably greater than the present production of coal tar on which a large part of the organic chemical industry is based.

3310. SUSTMANN, H. [Attempts to Change Properties of Kogasin by Compression up to 12,000 Atmospheres.] Brennstoff-Chem., vol. 21, 1940, pp. 246-250; Chem. Zentralb., 1941, I, p. 850; Chem. Abs., vol. 35, 1941, p. 7694.

Attempt to produce lubricating oil by polymerizing unsaturated hydrocarbons in Kogasin (I) by applying pressure. A (I)* fraction (b. 50°-250°) in a Pb- or Zn-plated Pb tube was compressed to 5,000 kg. per cm.² and 11,700 kg. per cm.² for 1-5 hr., and the change in η was noted. Inconclusive results were obtained. Experiments using thin Pt tubes are suggested as likely to yield more precise data.

SUTCLIFFE, H. T. See abs. 24.

SWIFT, A. H. See abs. 622.

3311. SYMONDS, F. L., LAUGHREY, P. W., SKINNER, L. C., BAICHELDER, H. R., AND DONATH, E. E. Synthetic

TADA, M. See abs. 2501.

TAGLANG, P. See abs. 2242.

TAHARA, H. See abs. 1907, 1909, 1910, 1911, 1912, 1913, 1914, 1927, 1928, 1929, 1930.

TAHARA, H., ISHIBASHI, T., AND KODAMA, S. Preparation of Isobutanol From Carbon Monoxide and Hydrogen. III. Influence of Alkali on the Copper-Chromium Oxide Catalyst. See abs. 3316.

TAHARA, H., ISHIBASHI, T., AND KODAMA, S. Preparation of Isobutanol From Carbon Monoxide and Hydrogen. IV. Results of Syntheses in Long Runs. See abs. 3317.

3313. TAHARA, H., TATUKI, Y., AND SIMIZU, J. [Catalytic Reactions of Carbon Monoxide and Hydrogen Under High Pressure. I. Synthesis of Isobutyl Alcohol.] Jour. Soc. Chem. Ind. (Japan), vol. 43, 1940, p. 82 B (in German); Chem. Abs., vol. 34, 1940, p. 6929.

In order to synthesize iso-BuOH, a mixture of 1 part CO and 2 parts H₂ under a pressure of 180 kg. per cm.² is conducted with velocities 120-800 l. per hr. over 30 cc. of 10 various catalysts at 450° and 500°. The liquid product contains, at best, 30% iso-BuOH. The yield decreases with the velocity with which the initial gas mixture is led over the catalysts and is dependent to a high degree on the reaction temperature.

3314. TAHARA, H., SAWADA, Y., AND KOMIYAMA, D. [Catalytic Reaction of Carbon Monoxide and Hydrogen Under High Pressure. II. The Influence of High Pressure on the Iron Catalyst Employed in the Synthesis of Benzene.] Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 38, 1941, pp. 184-195 (in German); Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, suppl., pp. 77-82; Chem. Zentralb., 1941, I, p. 2891; Chem. Abs., vol. 35, 1941, p. 3416.

Brief review of some of the earlier work. The same experimental methods were used as on the previous

Fuel Processes May Be Future Source of Utility Gas. Am. Gas Jour., vol. 171, No. 1, 1949, pp. 19-21; Am. Gas Assoc. Monthly, vol. 31, No. 7-8, 1949, pp. 18-20, 24.

Paper presented at the American Gas Association meeting, May 1949. The residual gas from both the coal-hydrogenation process and the Fischer-Tropsch is suitable for general use as a city gas. In the former case, the city gas produced in the normal operation of a 10,000-bbl.-per-day plant will amount to about 390,000 cu. ft. per hr. with a net heating value of 1,065 B. t. u. per cu. ft. To make this gas available for city gas consumption, the hydrocarbon steam-reforming section would be eliminated, and the size of the coal gasification section would be increased to such a point that it could produce an equivalent amount of H₂. With coal at \$3.56 per ton, the actual cost of the city gas would be \$0.44 per M. B. t. u. The value of the gas from the Fischer-Tropsch process roughly will equal that recovered from coal hydrogenation. Assuming that 1,000,000 bbl. per day of synthetic liquid fuels were to be produced and that 75% of this is suitable for city gas, 710,000,000 cu. ft. per day would be available, or about 90% of the total manufactured gas production of the entire United States in 1944.

3312. SZCZENIOWSKI, B. [Fuel Problems During 1935.] Przegląd Mechaniczny, vol. 2, 1936, pp. 5-6.

Characteristics of actual trends in various countries with special regard to polymerization of gases obtained by cracking, coal hydrogenation, Fischer-Tropsch synthesis, and from water gas are given.

SZEGO, P. See abs. 2447.

low-pressure investigation. The reaction was studied at 10, 50, and 100 kg. per cm.². The high pressures used with the Fe catalyst (composition: Fe+25% Cu+2% Mn+125% kieselguhr+15% H₂BO₃+2.8% K₂CO₃) formed considerable H₂O, which did not form in the low-pressure studies. At 10 kg. per cm.², the yield of benzene was greater than at atmospheric pressure, and the yield did not fall even when the stream velocity was doubled. The activity of the catalyst declined under this pressure even more rapidly than under atmospheric pressure. At pressures of 50 and 100 kg. per cm.², the yield of benzene fell very sharply, and a marked increase in the formation of CH₄ occurred.

3315. TAHARA, H., KOMIYAMA, D., KODAMA, S., AND ISHIBASHI, T. Preparation of Isobutanol From Carbon Monoxide and Hydrogen. II. Copper-Chromium Oxide Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, pp. 89-90; Chem. Abs., vol. 45, 1941, p. 2849.

Good yields (28-34%) of iso-BuOH were obtained when the catalyst contained 15-70 parts Cu per 100 parts Cr and 20 parts K₂CO₃. The best yield (34%) was with 25 parts Cu. This product also contained 29% MeOH and 6% EtOH and PrOH. (See also abs. 3313.)

3316. TAHARA, H., ISHIBASHI, T., AND KODAMA, S. Preparation of Isobutanol From Carbon Monoxide and Hydrogen. III. Influence of Alkali on the Copper-Chromium Oxide Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, pp. 90-91; Chem. Abs., vol. 45, 1951, p. 2849.

Varying amounts of K₂CO₃ and other K salts were added to the Cu-Cr (1:4) catalyst. The best yield (37%) of iso-BuOH was obtained with 70 gm. K₂CO₃ per 100 gm. Cu+Cr. Higher yields of total reaction product were obtained with K₂ZnO than with K₂CO₃, but the product contained more H₂O. Other K salts

gave poorer yields. With 248 gm. $K_2Mo_2O_7$, only CH_4 was recovered.

3317. —. Preparation of Isobutanol From Carbon Monoxide and Hydrogen. IV. Results of Syntheses in Long Runs. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, pp. 91-92; Chem. Abs., vol. 45, 1951, p. 2849.

Catalyst of Cu 1, Cr 4, and K_2CO_3 4 parts was heated at 400° and the gases passed over it at a pressure of 180 kg. per 3 cm^2 at the rate of 200 l. per hr. At the start, 44 cc. fluid per m. gas was obtained and at the end of 48 hr., only 19 cc. The concentration of iso-BuOH fell from 37 to 30% in 10 hr. and to 24% of the product in 100 hr. The concentration of MeOH increased with time. The products contained about 10% C:O compounds with a ratio of aldehydes to ketones of 4:1, and 12-16% hydrocarbons.

TAKEGI, H. See abs. 1485.

3318. TAKAHASHI, G. Equilibrium Between Austenite and the Carbon Oxides. Sci. Repts. Tohoku Imp. Univ., vol. 15, 1926, pp. 157-175; Chem. Abs., vol. 20, 1926, p. 2810.

As the temperature rises, the C content of the austenite in equilibrium with a given mixture of CO and CO_2 decreases, and the CO concentration in the gas in equilibrium with austenite of constant C content, or with austenite and cementite, increases. As the CO concentration of the gas increases at constant temperature, the C content of austenite in equilibrium with it increases until free cementite appears. As the temperature rises, the C content of austenite in equilibrium with FeO decreases; and the CO concentration in the gas in equilibrium with austenite and a Fe decreases, while that in equilibrium with austenite and FeO increases. Cementation does not occur when the CO concentration in the gas is less than that with which austenite and a Fe are in equilibrium. By means of cementation in CO, the temperature of the A₁ point was determined to be 726° .

TAKAZAWA, T. See abs. 1918, 1919, 1920, 1921, 1922, 1923, 1924, 1925, 1926.

TAKEGAMI, Y. See abs. 1904.

3319. TAKEI, M. Preparation of Raw Gas for Fischer Synthesis at Milke. Jour. Fuel Soc. Japan, vol. 16, 1937, pp. 87-88; Chem. Abs., vol. 32, 1938, p. 5904.

Satisfactory synthesis gas is obtained by mixing water gas with coke-oven gas, which has been subjected to CH_4 cracking in a high-temperature vertical stove. The heat required for CH_4 cracking is provided by the waste gas resulting from the Fischer process.

3320. TAKENAKA, Y. Destructive Hydrogenation of Synthetic Petroleum. I. Effect of Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 658-662; Chem. Abs., vol. 43, 1949, p. 2415.

Kogasin oil (synthesized from CO and H_2 under pressure) was fractionated into 3 portions distilling at 100° - 200° , 200° - 300° , and above 300° , respectively. Each portion was hydrogenated 5 min. in a rocking autoclave at 480° by using 20% Ni_2O_3 , MoO_3 , MoS_2 , or $Mo(PO_3)_2$, with or without kieselguhr as catalyst, and H_2 under 35 atm. initial pressure to yield gasoline. The effect of using various catalysts on the composition of the product was studied. The reaction yielded 53-67% oil containing 47-65% gasoline, which was composed of 5-9.5, 3.1-11.8, and 14-22%, respectively, unsaturated, aromatic, and naphthenic hydrocarbons, and the remainder was saturated hydrocarbons. With Ni_2O_3 on kieselguhr, a gasoline fraction containing mostly aromatic and naphthenic hydrocarbons was obtained, although the total oil fraction yield was small. MoS_2 and $Mo(PO_3)_2$ were second to Ni_2O_3 in producing the same result. The effect of using a carrier varied according to the catalyst used. Among the different

fractions of Kogasin oil, that which distilled at the highest temperature gave a product containing the largest amount of cyclic hydrocarbons.

3321. —. Destructive Hydrogenation of Synthetic Petroleum. II. Effect of Reaction Conditions. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 653-662; Chem. Abs., vol. 43, 1949, p. 2415.

Similar experiment was carried out by using 20% $Mn(PO_3)_2$ on kieselguhr as a catalyst and varying the initial pressure of H_2 , reaction temperature, and time to find the optimum conditions for obtaining gasoline of high octane no. Higher temperatures and less H_2 , or a longer reaction time at a lower temperature yielded a high-octane gasoline. By treating a fraction, boiling 200° - 300° , with 2.85% H_2 under 44 atm. initial pressure 3 min. at 500° , gasoline having an octane no. of 75.4 was obtained. Gasoline having a high octane no. can be obtained from oil rich in normal paraffins by proper treatment.

See abs. 2017, 2018.

TAKEZAKI, Y. See abs. 1894.

TAKIGUCHI, K. See abs. 1910.

3322. TAMMANN, G. [Transformation of Cementite at 210° .] Stahl u. Eisen, vol. 42, 1922, pp. 772-775; Chem. Abs., vol. 16, 1922, p. 3847.

Lack of linear change of properties in steel with C content raises the question whether primary cementite and pearlitic cementite are the same kind of crystals. In order to answer this question the transformation point of the 2 kinds is studied and found to be the same; the difference of the 2 kinds of cementite is, accordingly, one of grain size. In the discussion this conclusion is confirmed as a result of X-ray analysis of the 2 kinds of cementite.

3323. TAMMANN, G., AND BANDEL, G. [Heat Content and Specific Volume of Iron-Carbon Alloys.] Arch. Eisenhüttenw., vol. 7, 1934, pp. 571-578; Chem. Abs., vol. 28, 1934, p. 4356.

Literature on heat content, specific heat, and specific volume of Fe-C alloys and their changes in melting is compiled. Diagrams of state in 3 dimensions are constructed showing dependence of heat content and specific volume on C content and temperature. The 7-solid solutions must be considered, by their lattice parameters, as embedded solid solutions; the C atoms are situated between the lattice points, which are occupied only by Fe atoms, whereby the lattice is widened. The specific volume of Fe-C alloys $1,100^\circ$ - $1,650^\circ$ increases slightly with C content. Pressure has little influence on the temperature of the pearlite transformation.

3324. TAMMANN, G., AND EWIG, K. [Contribution to the Knowledge Concerning Cementite.] Ztschr. anorg. Chem., vol. 167, 1927, pp. 385-400; Chem. Abs., vol. 22, 1928, p. 570.

Temperature-magnetization curves of C steels, ranging 0.15-3.9% C, indicate an abrupt lowering in magnetizability at 200° - 220° . This lowering is proportional to the C content and, therefore, to the FeC content. Lowering of the magnetizability during the pearlitic transformation becomes less with increasing C content. Since FeC loses its magnetic properties at 210° , some of it was heated to various temperatures and temperature-magnetization curves were obtained. After heating FeC for 5 hr. at 500° , the curves showed no noticeable decrease at 210° . This indicates that after heating at 500° for 5 hr., FeC is completely decomposed into Fe and C. The probable effects of dissolved gaseous impurities, and of including the FeC in a structure of ferrite (as in steel), upon the decomposition temperature of FeC are discussed. The heat of transformation of FeC (magnetic-nonmagnetic variety) cannot exceed 0.02 cal. per gm. With a dil-

meter the increase in volume at the temperature of the magnetic transformation (200° - 215°) was 0.0714 mm. per gm. of FeC. This change in volume should produce noticeable changes in the physical properties of steels and, also, in white cast Fe. A study of the effect of the addition of Si, Mn, Ti, Al, and B upon the magnetic transformation temperature was undertaken. Al and Ti were without effect. 5% Si has little effect; 14% Si lowers the transformation temperature 100° ; 3% Mn lowers this temperature 100° ; 0.5% B lowers the temperature 200° .

TARAMA, K. See abs. 1892, 1915, 1916, 1917, 1918, 1919, 1920, 1921, 1922, 1923, 1924, 1925, 1926, 2196, 2197, 2200, 2201, 2202, 2203, 2204.

TARAMA, K., TATSUKI, Y., KASAI, K., AND TAKEGAMI, Y. Synthesis of Benzene From Carbon Monoxide and Hydrogen. LXVIII. Analysis of the Synthetic Oil by Fractional Distillation. (2). See abs. 1904.

TARAMA, Y. See abs. 1930.

TARN, W. H. See abs. 46, 51, 53c.

TASHIRO, E. See abs. 1896, 1900, 1901, 1902.

TATARSKI, E. S. See abs. 3267.

3325. TATEVSKAYA, E. P. [Effect of Water Vapor on the Rate of Reduction of Magnetite and Hematite by Carbon Monoxide.] Jour. Phys. Chem. (U. S. S. R.), vol. 14, 1940, pp. 349-356; Chem. Abs., vol. 36, 1942, p. 3760.

2.5-20% of H_2O vapor added to CO strongly retards the reduction of Fe_3O_4 at 900° , and especially at 500° ; the retardation is more pronounced if the Fe_3O_4 is already partly reduced. Reduction of Fe_3O_4 is not affected by H_2O at 500° or 900° unless Fe_3O_4 is already partly reduced. H_2O has no specific effect, it gives CO and H_2 with CO on Fe oxide catalysts, and its apparent action is due to CO_2 . CO_2 does not retard the reduction of Fe_3O_4 to FeO . The inhibition of the reduction of Fe_3O_4 can be accounted for by considering the competition between CO and CO_2 for the magnetite surface.

See abs. 567, 568.

3326. TATEVSKAYA, E. P., AND CHUFAROV, G. I. [Effect of Carbon Dioxide on the Velocity of Reduction of Magnetite and Hematite by Carbon Monoxide.] Jour. Phys. Chem. (U. S. S. R.), vol. 13, 1939, pp. 495-501; Chem. Abs., vol. 34, 1940, p. 8284.

Experimental data over the temperature range 400° - 900° and at gas pressures of 0.02-0.20 mm. Hg are given. The retarding effect of CO_2 on the initial stage of reduction of magnetite is considerable at 500° and negligible at 900° ; CO_2 does not affect the initial reduction of hematite, but, after a Fe_3O_4 surface layer has once formed, hematite behaves the same as magnetite.

3327. TATEVSKAYA, E. P., CHUFAROV, G. I., AND AXONOV, V. K. [Rates of Reduction of Iron Oxides.] Jour. Phys. Chem. (U. S. S. R.), vol. 24, 1950, pp. 385-393; Chem. Abs., vol. 44, 1950, p. 8200.

Although the equilibrium pressure, calculated, of O_2 over Fe_3O_4 is much greater than over Fe_2O_3 or FeO , all 3 oxides are reduced by H_2 at similar rates, showing that reduction is independent of dissociation and that reduction of FeO is not the slowest stage in the reduction of higher oxides. The surface area of the oxides, from N_2 adsorption at -195° , was 0.85, 0.86, and 0.60 m^2 per gm. for Fe_3O_4 , Fe_2O_3 , and FeO , respectively. The oxides were heated in H_2 , the H_2O formed was frozen out, and the rate v of reaction was calculated from the decrease in pressure p . In 1 experiment, v first increased to a maximum at 10-30% reduction and then decreased again. When the original $p(p_0)$ was 200 mm. Hg, the maximum v of Fe_3O_4 was about 7, 16, 37, and 95×10^{-4} gm. O_2 per gm. Fe_3O_4 and minimum at 350° , 400° , 450° , and 500° , respectively; the maximum

v of the other oxides were, for example, 10% less. At reductions below 10%, v was proportional to p_0^n , and the constant n was at 400° and 450° 0.68 and 0.83 for Fe_3O_4 , 0.68 and 0.76 for Fe_2O_3 , and 0.5 and 0.65 for FeO , when p_0 varied 0-320 mm. Hg. The apparent energies of activation were 16,500, 13,500, and 14,000 cal. per mol.

TATSUKI, Y. See abs. 1893, 1904.

TATSUKI, Y. See abs. 3313.

3328. TAUSSIG, J. H., JR. Theoretical Advantages of Low Air: Steam Ratios in Water-Gas Manufacture. Gas Age, vol. 85, No. 12, 1940, pp. 31-33, 40; Chem. Abs., vol. 34, 1940, p. 4886.

From the standpoint of generator fuel consumption, the lowest air: steam ratio that can be used and still supply enough heat for oil vaporization and fixing is most economical, because the lower ratios make cooler fires and promote the reaction: $C+2H_2O=CO+2H_2$, and retard the reaction: $C+CO=2CO$. The most economical point of operation may be found by plotting the cost of steam against the air: steam ratio and the cost of fuel against the air: steam ratio and selecting the air: steam ratio at which the sum of the costs is a minimum.

3329. TAYLOR, A. H. Sensitive Pressure Controller. Fuel, vol. 29, 1950, p. 262-264.

An instrument for insuring close and reliable pressure control in the Fischer-Tropsch synthesis is described. It is also an efficient oil-gas separator. Graphs show the sensitivity at gas flows up to 2,500 cu. ft. per hr. over a pressure range up to 60 atm. Illustration.

See abs. 1333.

3330. TAYLOR, E. H., AND TAYLOR, H. S. Hydrogenation of Ethane on Cobalt Catalysts. Jour. Am. Chem. Soc., vol. 61, 1939, pp. 503-509; Chem. Abs., vol. 33, 1939, p. 3755.

Rate of hydrogenation of C_2H_6 to CH_4 has been studied over a Co- ThO_2 -Cu-kieselguhr catalyst and upon 4 Co-MgO catalysts. The results indicate that Co lies between Cu and Ni in its activity for this reaction. The rate is inhibited by H_2 , but to a lesser extent than on Ni. The Co-MgO catalysts are markedly more active than the catalyst containing ThO_2 .

3331. TAYLOR, G. B., AND STARKWEATHER, H. W. Reduction of Metal Oxides by Hydrogen. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 2314-2325; Chem. Abs., vol. 24, 1930, p. 3944.

Method is described for studying the rate of reduction of metal oxides at temperatures below 500° in which the volume of H_2 consumed is measured. The oxides of Ni, Cu, Fe, and Zn were studied by this method. Fe_3O_4 gels are reduced to ferrous-ferric oxide at 350° and to metallic Fe at 450° . Ignited Fe_3O_4 is not appreciably reduced at 350° but goes to metal at 450° . Foreign metal interfaces with Fe_3O_4 accelerate the reduction of Fe. Al_2O_3 and Cr_2O_3 greatly retard the reduction of ferrous-ferric oxide. Fe_3O_4 gels show the glow phenomenon in H_2 at fairly low temperatures but not in air or vacuum. The thermodynamics of ZnO reduction in the presence of Cu are worked out, giving an explanation of the formation of α -brass.

TAYLOR, H. G. See abs. 3305a.

3332. TAYLOR, H. S. [Active Centers on Catalysts.] Ztschr. Elektrochem., vol. 35, 1929, pp. 542-549; Chem. Abs., vol. 23, 1929, p. 5395.

Measurements of heats of adsorption of gases on metal and metal oxide catalysts are discussed. The difficulty in explaining the observed maximum in heats of adsorption is considered. It is emphasized that the energy of activation of a surface reaction is dependent on the preparation of the contact substance. It is

possible that for a given reaction the energy of activation is smaller the more active the catalyst. Measurements of heats of adsorption together with reactions studied on poisoned and nonpoisoned catalysts demonstrate the existence of centers of different activity on a catalyst. A specific effect on the reacting molecules is exerted only by certain well-defined areas of the macroscopic surface.

3333. ———. Heterogeneity of Catalysts Surfaces for Chemisorption. *Advances in Catalysis*, Academic Press, Inc., New York, 1948, vol. I, pp. 1-26; *Chem. Abs.*, vol. 44, 1950, p. 5690.

Examination of the adsorption of H_2 on various oxide and metal surfaces.

3334. ———. [Effect of the Heterogeneity of Catalysts on Chemisorption and Chemical Kinetics.] *Jour. chim. phys.*, vol. 47, 1950, p. 1225; *Chem. Abs.*, vol. 44, 1950, p. 7132.

Taylor presents his current views on the heterogeneity of surfaces; he points out that the Langmuir, Brunauer-Emmett-Teller, Hüttig, Harkins and Jura adsorption theories all assume a uniform surface and the absence of interaction between adsorbed molecules. Strictly speaking, this cannot be true, however, and on the basis of recent work in his and other laboratories Taylor reemphasizes the importance of the Freundlich isotherm $v = kp^{1/n}$.

———. See abs. 414, 415, 699, 1162, 1339a, 1639, 2321, 2322, 2547, 2994, 3330, 3339, 3746.

3335. TAYLOR, H. S., AND BURNS, R. M. Adsorption of Gases by Metallic Catalysts. *Jour. Am. Chem. Soc.*, vol. 43, 1921, pp. 1273-1287; *Chem. Abs.*, vol. 15, 1921, p. 3922.

Measurements of the adsorption of H_2 , CO, and CO_2 and C_2H_4 by finely divided Ni, Co, Fe, Cu, Pd, and Pt were made. Adsorption by a metallic catalyst is not like adsorption by such inert substances as charcoal and silica gels. It is specific, and saturation capacity is reached at low partial pressures of the gas. It is a surface phenomenon involving electronic rearrangements in both catalyst and adsorbed gas. Methods of preparation, which produce good metallic catalysts also produce metals with high powers of adsorption for gases whose reaction they catalyze, but the temperature of maximum adsorption is often lower than temperature of maximum chemical activity. This probably means that a free evaporation of both reactants and resultants is necessary for rapid chemical action. The greater the adsorption the lower is the temperature at which catalytic action begins.

3336. TAYLOR, H. S., AND KISTIAKOWSKY, G. B. Methanol Catalysts. I. *Jour. Am. Chem. Soc.*, vol. 49, 1927, pp. 2468-2476; *Chem. Abs.*, vol. 21, 1927, p. 3804.

Adsorptions of H_2 , CO, and CO_2 on 2 MeOH catalysts, ZnO and ZnO-Cr₂O₃, were measured at 0° and 100°. In order to obtain reproducible results, it was necessary to clean the surface of H_2 O and CO_2 by preliminary evacuation at 400°. Both these catalysts had adsorptive capacities considerably greater than those of most metal catalysts. The adsorption of both H_2 and CO is large at very low pressures and rapidly reaches saturation capacity independently of further pressure increase. The experiments indicate that the heat of adsorption is of the same order as that on metal catalysts. The mixed oxide catalyst shows greater adsorptive capacity than the ZnO. The results are consistent with the known facts concerning MeOH synthesis on these catalysts.

3337. TAYLOR, H. S., AND LIANG, S. C. Heterogeneity of Catalyst Surfaces for Chemisorption. I. *Zinc Oxide*. *Jour. Am. Chem. Soc.*, vol. 69, 1947, pp. 1306-1312; *Chem. Abs.*, vol. 41, 1947, p. 5712.

New technique for determining adsorption isobars was applied to the study of the adsorption of H_2 by

ZnO over the temperature range 77°-600° K. It reveals desorption of chemisorbed H_2 on raising the temperature through certain temperature ranges, followed by re-adsorption at still higher temperature. The data indicate a marked heterogeneity of the ZnO surface for the adsorption of H_2 that must be taken into consideration in attempting to evaluate energies of activation for adsorption and catalysis.

3338. ———. Heterogeneity of Catalyst Surfaces for Chemisorption. II. *Zinc Oxide-Chromic Oxide, Manganous Oxide-Chromic Oxide, Chromic Oxide Gel*. *Jour. Am. Chem. Soc.*, vol. 69, 1947, pp. 2989-2991; *Chem. Abs.*, vol. 42, 1943, p. 1793.

As described in the previous paper in this series, the techniques of measuring chemisorption with increasing and decreasing temperatures at constant pressure were applied to a study of ZnO-Cr₂O₃, catalysts and Cr₂O₃ gel. These substances reveal heterogeneity of surface. MnO-Cr₂O₃, catalysts do not show desorption-adsorption phenomena on raising the temperature. The isobar on decreasing temperature consequently was horizontal over a considerable temperature range. The surface, nevertheless, exhibits a partial heterogeneity. The criterion of "pumping-off at temperature" was shown to be doubtful in distinguishing van der Waals' and chemisorption of H_2 in certain temperature ranges with these catalysts.

3339. SADER, H., AND TAYLOR, H. S. Heterogeneity of Catalyst Surfaces for Chemisorption. III. *Metallic Nickel*. *Jour. Am. Chem. Soc.*, vol. 72, 1950, pp. 1168-1175; *Chem. Abs.*, vol. 44, 1950, p. 5190.

Heterogeneity of the surfaces of 6 different Ni catalyst preparations was confirmed with the technique devised by Taylor and Liang (abs. 3338) and H_2 as the adsorbate. The adsorption at -195° were analyzed to determine the relative amounts of van der Waals adsorption and chemisorption of H_2 , and to show that different preparations adsorb different relative amounts of the 2 types. The velocity of the H-D exchange reaction on Ni-Cr₂O₃ and Ni-ThO₂ was studied to support these findings. There are marked differences in rates with activation energies of 0.45 and 2 kcal., respectively. The data do not support an interpretation based either on solubility of H_2 in the lattice or an exothermic entry of H_2 into the Ni lattice at temperatures -195° to -78°.

3340. TAYLOR, H. S., AND NEVILLE, H. A. Catalysis in the Interaction of Carbon With Steam and With Carbon Dioxide. *Jour. Am. Chem. Soc.*, vol. 43, 1921, pp. 2035-2071; *Chem. Abs.*, vol. 16, 1922, p. 522.

Steam was passed over C at 490°, 525°, and 570° and the volume, and composition of the gases evolved were determined both in the presence and absence of catalysts. The reaction is (a) C + 2H₂O = CO + 2H₂. The amount of CO in the emergent gases was hardly measurable. This reaction takes place in 2 steps (b) C + H₂O = CO + H₂, and (c) CO + H₂O = CO₂ + H₂, of which (c) is the slower. Good catalysts for (c) such as Fe oxide do not affect the velocity of (a); hence (c) reaches equilibrium under these conditions even in the absence of catalysts. Many substances of which K₂CO₃ is best are powerful catalysts for (a). The same substances are found to catalyze the reaction (d) C + CO₂ = 2CO. Adsorption measurements show that these catalysts increase the adsorption of CO₂ by charcoal. The results conform to the view that a surface complex C₂O₂ is formed and the catalysts hasten the decomposition of this complex, thus cleaning off the surface for further adsorption of CO₂.

3341. TAYLOR, H. S., AND OGDES, G. Adsorption of Hydrogen and of Carbon Monoxide on a Surface of Zinc and Molybdenum Oxides. *Trans. Faraday Soc.*, vol. 30, 1934, pp. 1178-1190; *Chem. Abs.*, 29, 1935, p. 2418.

Mixture of ZnO with excess of Mo oxide exhibits van der Waals' adsorption in a low-temperature range and activated adsorption in a high-temperature range with both H_2 and CO. The decreased extent of activation adsorption and the increased activation energy when Mo oxide is mixed with the ZnO explains why the Mo oxide reduces the catalytic action of ZnO in the MeOH synthesis.

3342. TAYLOR, H. S., AND SICKMAN, D. V. Adsorption and Reactions at Surfaces of Zinc Oxide. *Jour. Am. Chem. Soc.*, vol. 54, 1932, pp. 602-613; *Chem. Abs.*, vol. 26, 1932, p. 1852.

Difficulties in measurement of the velocity of decomposition of alcohols on ZnO surface are discussed. The importance of the adsorption of H_2 O in the decomposition of alcohols is shown. Evidence for an activated adsorption of H_2 O on ZnO is given. The velocity of adsorption of H_2 by ZnO was measured in the range 0°-360°; isotherms were obtained at -191° and -78.5°. The heats of adsorption of 2 types of adsorption of H_2 by ZnO were determined. A theory of activated adsorption is developed mathematically, which gives expressions for the temperature of maximum adsorption. Methods of calculating the activation energy and heat of adsorption are given.

TAYLOR, J. See abs. 2041.

TAYLOR, P. S. See abs. 1099.

3343. TAYLOR, R. Present Position as Regards Production of Liquid Fuels From Water Gas. *Chem. and Ind.*, vol. 50, 1931, pp. 580-584; *Chem. Abs.*, vol. 25, 1931, p. 4333.

Review of the development of the synthetic liquid fuel processes—MeOH, higher alcohols, synthol, gasoline.

3344. ———. Catalytic Syntheses With Carbon Monoxide and Hydrogen Under Pressure. *Jour. Chem. Soc.*, 1934, pp. 1429-1431; *Chem. Abs.*, vol. 29, 1935, p. 115.

With 3 catalysts [Mn-Cr-Rb oxide (I), Zn-Mn-K-Co oxide (II), and Cu-Mn oxide-Co sulfide (III)] the weights of the constituent alcohols per kgm. of crude product were found as follows (the data for (III) were obtained with product that had been hydrogenated, and aldehydes and acids had been removed from the other 2 products before distillation of the alcohols) (the order is (II), (I), (III)): MeOH 230, 420, 198; EtOH 200, 12, 86; PrOH 50, 43, 17; iso-BuOH 3, 69, 11; BuOH 16, —, 4; β -methylbutyl alcohol 2, S, 1.5; AmOH, 6, —, 1; β -methylamyl alcohol —, 6.5, —; hexyl alcohol 2, —, —; heptyl alcohol <1, —, —; residue 1, 89, 1.5. (III), which contained Co but no alkali, produced alcohols higher than C₆, the majority of which had straight chains, and (I), which contained alkali but no Co, gave higher alcohols, a large proportion of which had branched chains, while (II) gave both alcohols.

3345. ———. High-Pressure Synthesis of Aliphatic Compounds. *Gas World*, vol. 104, No. 2696, Coking Sec., 1936, pp. 38-42; *British Chem. Abs.*, 1936, B, p. 440.

Review of the patent literature and of work carried out at the Chemical Research Laboratory on the high-pressure synthesis of MeOH from CO and H_2 , of BuOH from EtOH and CO, and of AcOH from MeOH and CO.

———. See abs. 2316, 2317, 2319.

TAYLOR, R. S. See abs. 1744.

TAYLOR, W. J. See abs. 3589.

3346. TEBBOTE, J. A. Decomposition of Carbon Monoxide by Nickel Catalysts. *Reaction Mechanism Between 250° and 450°*. *Jour. Soc. Chem. Ind.*, vol. 67, 1948, pp. 62-66.

Principal factors involved in the catalytic formation of CH₄ from water gas have been described recently. A

major difficulty encountered was the progressive deposition of C on the Ni-ThO₂-kieselguhr catalyst used. An attempt is made here to ascertain the mechanism of the formation of C and how to minimize it. It was found that unsupported and unpromoted Ni catalysts, derived from precipitated NiCO₃, showed little activity for the decomposition of CO at all temperatures between 250° and 450°. The presence of ThO₂ and kieselguhr in a Ni catalyst prepared from the precipitate NiCO₃ caused a marked increase in the rate of decomposition of CO at the same temperatures. Elementary C formation occurred on Ni catalysts at all temperatures from 250°-450°, being least at 250° and greatest at 325°-350°. The Ni of such promoted and supported Ni catalysts was converted almost quantitatively to Ni₃C at 250°. Above this temperature, carbide formation was incomplete. Decomposition of Ni₃C in the presence of ThO₂ and kieselguhr occurred above 250° and was rapid at 300°. The proportion of C combined as carbide decreased with increasing temperature, but some persisted at 450°. When using promoted and supported catalysts for CH₄ synthesis from CO and H_2 , the conditions prevailing at the inlet end of the catalyst bed were very favorable for elementary C formation. The results were accounted for by 2 reactions: 3 Ni + 2 CO = Ni₃C + CO, and Ni₃C = C + 3 Ni. The latter reaction may have occurred in 2 stages with the formation of a lower carbide Ni₃C, but evidence here was incomplete. ———. See abs. 304.

3347. TECHNICAL OIL MISSION. [Operation Costs in the Synthesis-Gas Production in Rheinpreussen.] *TOM Reel 43*, 1942, pp. 260-267; *Bureau of Mines Transl. T-154*, 1946, 6 pp.; *TOM Reel 237*.

Operating costs are computed for 4 different types of plants and are broken down for each item of operating expense.

- I. Water-gas plant—1,440,000 m³ water gas per day.
 - Coke at 20 RM per ton:
 - Water gas, 1.818 pf. per m³
 - CO + H₂, 2.075 pf. per m³
 - Coke at 17.50 RM per ton:
 - Water gas, 1.635 pf. per m³
 - CO + H₂, 1.875 pf. per m³
- II. Gasification of coal fines—1,440,000 m³ water gas per day.
 - Coal at 14 RM per ton and O₂ at 0.025 RM per m³:
 - Water gas, 1.045 pf. per m³
 - CO + H₂, 1.69 pf. per m³
- III. Reforming of coke-oven gas—356,000 m³ reformed gas per day.
 - Gas at 0.017 RM per m³:
 - Reformed gas, 1.69 pf. per m³
 - CO + H₂, 1.93 pf. per m³
 - Gas at 0.013 RM per m³:
 - Reformed gas, 1.375 pf. per m³
 - CO + H₂, 1.61 pf. per m³
- A. 65% water gas + 35% reformed gas.
 - Coke at 20 RM per ton and coke-oven gas at 0.017 RM per m³:
 - Synthesis gas, 1.769 pf. per m³
 - CO + H₂, 2.035 pf. per m³
 - Coke at 17.50 RM per ton and coke-oven gas at 0.013 RM per m³:
 - Synthesis gas, 1.543 pf. per m³
 - CO + H₂, 1.775 pf. per m³
- B. 70% water gas from powdered bituminous coal + 30% reformed gas.
 - Coke-oven gas at 0.017 RM per m³:
 - Synthesis gas, 1.487 pf. per m³
 - CO + H₂, 1.770 pf. per m³
 - Coke-oven gas at 0.013 RM per m³:
 - Synthesis gas, 1.392 pf. per m³
 - CO + H₂, 1.660 pf. per m³

IV. Gasification of powdered coal—direct production of synthesis gas $\text{CO}:\text{H}_2=1.2-1,440,000 \text{ m}^3$ per day, coal at 14 RM per ton and O_2 at 0.025, RM per m³.
Synthesis gas 1.37 pf. per m³.
 $\text{CO}+\text{H}_2$, 1.69 pf. per m³.

3348. — Fischer-Tropsch Use of Iron Catalyst. TOM Reel 26, bag 2463, document 9, frames 900,000,232-900,000,333 (particularly 286), Mar. 31, 1943.

X-ray investigations, made by Dr. Herbst and Dr. Halle on the Fe catalyst containing Cu, revealed that the Cu, besides aiding in the reduction of the catalyst, played another quite important role in the synthesis. It was found in examining the standard catalyst that a new hexagonal carbide Fe_3C occurred, not yet described in the literature, which appeared to be necessary to the high activity of the catalyst. This new hexagonal carbide, as Dr. Herbst discovered, becomes transformed in course of time, particularly at the higher temperatures, into the carbide Fe_3C already identified by Hugg. This transformation is retarded greatly by the addition of Cu so that it is regarded as a stabilizer in one of the intermediate states of the catalyst occurring during the synthesis. For example, the addition of 2% Cu raises the conversion temperature about 50°.

3349. — [Experience With the Semicommercial Synol Research Plant ME 458, Leuna Works, Oct. 10, 1944.] Transl. of German documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis. Part II, 1946, pp. 41-59; TOM Reel 56, bag 3979, item 73.

Detailed descriptive matter covering catalyst reduction, synthesis apparatus, CO_2 extraction, activated C adsorption, and distillation units. The catalyst is the standard fused Fe type (WK 17) of particle size 0.5-1.0 mm. and reduced at 450° at a space velocity of 1:2,000 of H_2 . The synthesis is performed by recycling at a throughput of 1:2,000 or 3,000 m³ of gas per m³ of catalyst per hr. with a gas conversion of 150 m³ per m³ of catalyst per hr. The yields amount to 170 gm. of products heavier than C_2 per m³, of which 35 gm. are gasol and 30 gm. paraffins boiling above 400°. The alcohol content in the lower-boiling fractions is 50-65%; from about C_4 upward the alcohol content declines, at C_8 about 30-40% of alcohols are obtained. The sum of the alcohols and olefins declines from 80% in the lower fractions to 65% in the boiling range of C_8 alcohols. The alcohols are primary and straight chain, the olefins likewise. The higher fractions contain esters to about 10% in the region of C_8 alcohols to 20% in the region of C_{12} alcohols. The content of the aldehydes and ketones in all fractions amounts to 1-2%.

3350. — Combined Intelligence Objectives Subcommittee Investigation of Ruhr Synthetic Oil Plants. TIC Rept. 17; Nat. Petrol. News, vol. 37, No. 45, 1945, pp. R-361-364.

Summary report of the visit to 7 plants using the Fischer-Tropsch process and to 3 using the hydrogenation process. No new developments were found to offset the economic disadvantages of both processes. Indications were that the German government had discontinued the construction of Fischer-Tropsch plants and was planning to build additional hydrogenation plants. The Ruhr plants were found to be using the ordinary Co-Th-Mg-kieselguhr catalyst. It seems clear that no German plants have been using the Fe catalyst but that it was to be used in a projected Italian plant. The Fe catalyst consists of 100 parts Fe, 2.5-4 Cu, 10 lime, and 15 kieselguhr and is prepared from the nitrates by precipitation with CO_2 .

Something was learned of the Oxo process for making alcohols by the Fischer-Tropsch process. Fischer-Tropsch C_2-C_7 olefins are treated at 140° and 150 atm. over a Co catalyst to produce aldehydes, which are reduced to alcohols over a Ni catalyst at 180° and 150 atm. The alcohols are converted into sulfonic ester soaps.

3351. — Thyssen-Galoesy Process. TOM Reel 65, frames 1-4, May 1945; Bureau of Mines Transl. T-402, Aug. 21, 1947, 3 pp.; TOM Reel 274, frames 1113-1115.

This process applies O_2 instead of air-blast for the complete gasification of solid fuel. It carries out the combustion in 2 stages with regulation of temperature, so that the refractory lining of the shaft is not destroyed by excess heat. An industrial-scale producer was installed and operated during the war and gave full satisfaction. Many advantages are quoted, among which are highly increased output in comparison with other plants (100,000-1,000,000 m³ per day in a single unit), high thermal efficiency, continuous working, utilization of cheap fuels, recovery of large amounts of low-temperature tar, and cheap gas for industrial heating and synthesis purposes. It is especially applicable in blast furnaces for the reduction of Fe ore.

3352. — [Hydrocarbon Synthesis With Iron Catalysts, Leuna Works, Apr. 5, 1940.] Transl. of German documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis. Part II, 1946, pp. 27-40; TOM Reel 134, item IB-23 (1st half).

Details are presented of the experimental investigation of 3 Fe catalysts: A fused Fe catalyst (997); a sintered Fe catalyst (Michael); and a Leuna NH_3 catalyst (WK 17), each reduced with H_2 at atmospheric pressure at temperatures 450°-550° for relative periods of 5-15 days. The converters were tube furnaces (the tubes 15 mm. diam.) with Dowtherm as the heat transfer medium. A synthesis gas of composition $\text{CO}:\text{H}_2=1:2.6$ was used, except when operating at 20 atm. when the composition was 1.2:1. Reduction at the lower temperatures produces more active catalysts, although not much is gained by going below 450°. When 2 catalysts of the same composition but reduced at 2 different temperatures were used, the one reduced at the lower temperature gave a lower-boiling product than the one reduced at the higher temperature. Higher space velocity and synthesis temperature also have a tendency to increase the yield of low-boiling constituents. In comparing the products formed on Co catalysts at middle and atmospheric pressures and a space velocity of 100 with those produced from a sintered Fe catalyst at 20 atm. and a space velocity of 200, it is seen that the latter gives better benzene yields than the former. An essential feature in the synthesis with Co is the comparatively high yield of paraffins in the benzene fraction (86% paraffins, 14% olefins), whereas the products from the Fe catalyst contain considerably greater amounts of unsaturates (approximately 50% olefins, 45% paraffins). The effect of this increased olefin content is to raise the octane number of the benzene fraction. Of 3 catalysts examined, a Co catalyst, WK17 and 997, the latter produced the highest olefin content with the highest octane number (71%, as compared with 15 and 48% and 63.5%, as compared with 25 and 57%). It is pointed out, however, that factors other than the olefin content influence the octane number. In general, for the same olefin content of the benzene fraction, a high reaction temperature, a high space velocity, and an active catalyst, in other words, all factors that favor the formation of low-boiling constituents, will yield a product having the highest octane number. Also, an increase in the olefin content is accompanied by a decrease in the boiling point of the product. Some data

are presented on the behavior of several fused Fe catalysts under specific synthesis conditions of 19 atm. pressure and 200 space velocity, and X-ray investigations were made to determine the nature of C deposition on the catalyst. It is believed that it takes place according to the equation $2\text{CO}\rightarrow\text{CO}_2+\text{C}$ and $4\text{CO}+3\text{Fe}\rightarrow\text{Fe}_3\text{O}_4+\text{C}$. A 2-stage operation was performed with a Co catalyst in the second stage at atmospheric pressure. The result was a conversion of 86% and a total yield from both stages of 135-150 gm. per m³ of water gas.

3353. — [Middle-Pressure Synthesis With Iron Catalysts, Sept. 9, 1939.] Transl. of German documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis. Part II, 1946, pp. 11-21; TOM Reel 101, Doc. PG-21, 578-NID.

Reviews historical development of the Fe catalyst. It is possible to point out that Fe catalysts, which are properly pretreated with CO and are operated at slightly elevated pressures, are capable of converting a theoretical mixture of CO and H_2 into hydrocarbons over a very long period. The total yields compare very closely to those obtained from Co catalysts, therefore, it now appears feasible to replace Co by Fe in the synthesis of hydrocarbons from CO and H_2 . Except for traces of alkali, the new Fe catalyst contains no additional material. It must, however, be inducted at approximate atmospheric pressure and above 250° over a period of 24 hr. The synthesis itself is best carried out at pressures 10-20 atm. and at maximum working temperatures of 230°-240°, with a synthesis gas containing CO and H_2 in the ratio of 3:2. Higher pressures necessitate higher operating temperature, and, with water as the cooling liquid, heavier pressure apparatus is required. Without regeneration of the Fe catalyst, constant yields of 150 gm. of liquid, gasol, and solid hydrocarbons per N m³ of synthesis gas are obtained indefinitely. The liquid hydrocarbon products contain approximately 66% of a benzene fraction boiling below 180° and 20% at 180°-300°. The content of solid paraffin is about 5%. In general, $\frac{2}{3}$ of the benzene fraction consists of unsaturated hydrocarbons and $\frac{1}{3}$ of saturated hydrocarbons, density 0.7 at 15°, octane number (I. G. Farbenindustrie-test engine) about 60. The benzene can be improved materially by following the synthesis with a polymerization of the primary unsaturated hydrocarbons, thus raising the octane No. to 67; by adding 0.7 cc. of tetraethyl lead per l., the octane No. is raised to 77.

3354. — [Middle-Pressure Synthesis With Iron Catalysts.] Transl. of German documents on the Development of Iron Catalyst for the Fischer-Tropsch Synthesis. Part II, 1946, pp. 21-24; TOM Reel 101, Doc. PG-21,578-NID.

This summary was made some time after September 1940, when plans were being made to modify the equipment for use with the Fe catalyst at temperatures below 225° and pressures not above 10 atm. Certain factors influencing the synthesis at lower temperatures are presented. A very active catalyst must be used, such as can be obtained by precipitation from an Fe-salt solution, having added thereto a promoter such as 1% or less of Cu and about 0.25% of alkali. Proper induction of the catalyst is required by using CO-rich gases at low pressures and a higher-than-synthesis temperature. The synthesis temperature should be carried out at a maximum pressure of 8-10 atm. and with a H_2 -rich synthesis gas. Under such conditions, conversion takes place at lower temperatures. For example, with a gas mixture of $\text{CO}:\text{H}_2=1:10$ conversion took place at 130°, and, at 140°, it amounted to 38% with a gas contraction of 12%; with

a ration of 1:4, the synthesis temperature varied between 180°-200°, therefore quite comparable to the conditions of the CO synthesis. Fe catalysts produce reaction products that contain larger quantities of gasol and oxygenated organic compounds, than do Co catalysts. Multistage operation or recycling is the most economical method; the higher the H_2 content of the gas, the more stages are recommended.

3355. — Thermodynamic Expressions for the Formation and Stability of Hydrocarbons. TOM Reel 134, item Ib-1; Bureau of Mines Transl., February 1947, pp. 1-8; TOM Reel 259, item 16.

Temperature range for which the formation of various hydrocarbons, saturated and unsaturated, from $\text{CO}+\text{H}_2$ is possible, is determined by consideration of the free energies of formation of the reactants and products. Calculations are carried over a range of pressures 1-100 atm. The conditions of thermodynamic stability are applied to consideration of condensation and decomposition reactions.

3356. — Thermodynamics of the Fischer-Tropsch Synthesis. TOM Reel 134, item Ib-2; Bureau of Mines Transl., February 1947, pp. 9-31; TOM Reel 259, item 16.

Theoretically obtainable yields at equilibrium for the synthesis of butane and octane from CO and H_2 were computed by standard thermodynamic methods. The effect of variations of temperature, pressure, and synthesis-gas composition on the theoretical yield were investigated.

3357. — Translations of German Documents on Mathematical Expressions for Thermodynamic Relationships and the Calculation of Yields in the Fischer-Tropsch Synthesis. Bureau of Mines Transl., February 1947, 78 pp.; TOM Reel 259, item 16.

Report consists of 4 translations of Technical Oil Mission Reel 134, Documents Ib-1, Ib-2, Ib-3, and Ib-4, identified, respectively, as: Thermodynamic Expressions for the Formation and Stability of Hydrocarbons, 8 pp.; Thermodynamics of the Fischer-Tropsch Synthesis, 23 pp.; Calculation of Gas Consumption and Synthesis Course in the Hydrogenation of CO, 38 pp.; Calculation of Yield for Higher Hydrocarbons Based on Recent Methods, 9 pp.

3358. — Winkler Method of Gasification. TOM Reel 128, LU II 84; Bureau of Mines Transl. T-400, Aug. 14, 1947, 6 pp.; TOM Reel 274, frames 1,095-1,100.

Theory and operation together with operating data are presented. This process permits the gasification of a wide range of fuels with maximum efficiency. Its specific gas production amounts to 1,000-4,000 m³ per m² of cross section of the shaft per hr., as compared with, at most, 800-1,000 m³ in the modern rotating-grate gas producer. It has the further specific advantage of permitting the production of various types of gases, depending on the choice of gasifying agent and the style of operation. A diagram is shown.

3359. TEICHNER, S. [Evolution of Surface Area of Fischer Catalysts During Reduction.] Compt. rend., vol. 227, No. 8, 1948, pp. 478-480; Chem. Abs., vol. 43, 1949, p. 27.

It has been shown by other workers that interaction between Ni or Co oxides and kieselguhr used as catalyst support occurs to some extent. Visser and de Lange found evidence for the formation of Ni hydrosilicate bonds by X-ray diffraction studies. Data are presented in this paper for surface area changes of a Ni-kieselguhr catalyst on heating in vacuum and reduction:

Treatment	Weight loss, percent	Surface area	
		M. ² per gm. of catalyst after pre-treatment	M. ² per gm. original catalyst
Evacuated 26 hr. at 20° C.	4.3	29	27
Evacuated 16 hr. at 120° C.	11.0	39	35
Reduced in H ₂ at 450° C. for 18 hr., followed by evacuation at 180° C. for 48 hr.	22.8	87	67

The authors postulate a laminar or montmorillonite structure for the metal oxide-kieselguhr complex of the unreduced catalyst. The increase in area on heating or reduction is not a direct consequence of this structure but is due to holes formed by removal of O₂, H₂O, and CO₂ during the heating or reduction. However, the laminar structure does tend to prevent the collapse of the pore system and sintering. These catalysts are prepared as basic carbonates of the active metals, and H₂O and CO₂ result from their decomposition.

3360. — [Choice and Role of Kieselguhr as Support of Fischer Catalysts.] *Compt. rend.*, vol. 228, 1949, pp. 1,644-1,646; *Chem. Abs.*, vol. 43, 1949, p. 8,830.

Three commercial kieselguhrs—crude Filter-Cel, acid-treated Filter-Cel, and crude Hyflo-Super-Cel—were subjected to thermal and alkaline treatment and loss in weight, density, and specific surface were determined. As the result of such considerations, the reactivity of a kieselguhr may be defined as the % of silica capable of being dissolved warm in a 5% solution of Na₂CO₃, which dissolves the amorphous or very finely divided silica. The efficiency of the kieselguhr in a Fischer catalyst is linked to the quantity of reactive silica that it initially contains or which it is possible to generate by acid treatment, as well as to the real surface of this reactive silica. The formation of hydrosilicates with foliated structure can, in fact, be promoted only by this type of silica.

3361. — [Analogies of Texture Between Activated Montmorillonites and Certain Catalysts.] *Jour. chim. phys.*, vol. 47, 1950, pp. 244-252; *Chem. Abs.*, vol. 44, 1950, p. 7635.

Adsorption results are summarized. Adsorption studies with N₂ and hydrocarbons were made of 6 Fischer-Tropsch catalysts. The loss in weight, the density as determined by He, and the surface areas are given for the following thermal treatments: Desorption under vacuum at 20°, desorption under vacuum at 150°, and reduction at 450° and desorption under vacuum at 150°. In 4 cases, the reduced catalysts exhibited much greater surface areas than the catalysts subjected only to a vacuum treatment at 20° or 150°. Results are tabulated for the surface area of the support, and the surface area of the catalysts impregnated on these supports before and after reduction for kieselguhr subjected to the following treatments: Treated with mineral acids, untreated support, treated with 5% Na₂CO₃. The surface area of the catalysts was greater than those of the supports. The initial surface areas of the support did not determine the surface area of the catalyst after reduction. The difference between the total adsorption of N₂ and CO at -195° was utilized to determine the fraction of metal exposed at the surface. The results are given for 4 catalysts. The fraction of surface covered by metal atoms ranged 0.35-0.65.

3362. — [Kieselguhrs of the Type Utilized as Support for Catalysts.] *Jour. chim. phys.*, vol. 47, 1950, pp. 229-232; *Chem. Abs.*, vol. 44, 1950, p. 7635.

Following properties of raw kieselguhr, kieselguhr treated with HCl and HNO₃ and calcined kieselguhr

were determined after different thermal treatments: Loss in weight after etching in Na₂CO₃, density, and specific surface as determined by adsorption of N₂ and CO at -195° and C₂H₆ at 0°. The kieselguhr treated with acids had approximately 50% greater specific surface than the raw kieselguhr. The specific surface of the calcined kieselguhr was only 11% as great as that of the untreated kieselguhr. Treatment with 5% Na₂CO₃ reduced slightly the surface area of the raw kieselguhr, but the same treatment decreased by 50% the surface area of the acid-treated kieselguhr. Presumably the acid treatment caused the formation of siliceous gel, which was soluble in Na₂CO₃. Discusses significance of the results to the activity of supports for catalysts used in the Fischer-Tropsch process.

3363. TEICHNER, S., AND PERNOUX, E. [Ultrasonic Fractionation of a Kieselguhr Carrier of a Fischer Catalyst.] *Compt. rend.*, vol. 230, 1950, pp. 1063-1064.

Suspension of an acid-treated kieselguhr (Filter-Cel) in distilled H₂O was subjected to an ultrasonic treatment ($\nu=970,000$). 2 fractions were obtained: One (12% of the initial weight of the kieselguhr) was a stable dispersion; the other remained precipitated on the bottom of the vessel. The specific surface, determined by absorption of N₂ at 195°, of the dispersed fraction was 40 m.² per gm., that of the initial acid-treated kieselguhr 27 m.² per gm. Besides, treatment with a 5% H₂O solution of Na₂CO₃ involved losses in weight of 21.6 and 14.5%, respectively. Examination under the electronic microscope revealed an extensive flocculent appearance for the dispersed fraction and considerably less so for the same fraction treated with carbonate. The precipitated fraction had a specific surface of 15.2 m.² per gm. and a loss in weight by the carbonate treatment of 9%. The properties were similar to those of a kieselguhr untreated with acid. The ultrasonic treatment, thus, furnishes further proof of the formation by the acid treatment of kieselguhr of a silica gel of flocculent appearance with a broad specific surface, and easy reaction with Na₂CO₃. Such a gel is formed for the most part in the dispersed phase of ultrasonic treatment.

3363a. — Texture and Surface Area of Kieselguhrs After Various Treatments. *Clay Minerals Bull.*, vol. 1, 1951, pp. 145-150; *Fuel Abs.*, 1952, abs. 4949.

Properties of raw and acid-treated Filter-Cel and Hyflo-Super-Cel characterize their ability to combine with the other constituents of catalysts. Their degree of "reactivity" was determined and compared with specific surface and appearance in the electron microscope. Densities and adsorption isotherms of N₂ at -195° were determined experimentally and surfaces calculated by the methods of Brunauer, Emmett and Teller. Attack by hot 5% Na₂CO₃ solution, which was used to measure the "reactivity," had not the same effect for all samples. Loss of silica, brought about by a small part of the kieselguhr dissolving in the carbonate solution, was nearly proportional to the initial specific surface of the samples. The specific surface of acid-treated Filter-Cel fell from 27-14 m.² per gm. but after alkaline attack, that of crude Filter-Cel was only slightly reduced. In the 1st case, the treatment had caused departure of a "reactive" silica with large surface formed by the acid treatment; in the 2d case, the "reactive" but low surface silica removed by alkaline treatment probably owed its solubility only to its finely divided state. Photographs of Filter-Cel treated with mineral acids and then by Na₂CO₃ are very different from those of Filter-Cel treated with mineral acids alone. The appearance of Filter-Cel treated by Na₂CO₃ alone is little different from that of the initial Filter-Cel. Thus acid treatment of crude kieselguhr causes the formation of a large surface silica gel which increases the total specific surface of the carrier. This

gel is eliminated during alkaline treatment and the specific surface of the substance diminishes by 50% and approaches that of the crude product. Formation of a hydrosilicate with flaky structure similar to that of montmorillonite is related to the possibility of combination of this "reactive" fraction of the kieselguhr which is used as a carrier. The conditions of formation of hydrosilicates in the catalyst mass of the Fischer process are different from the ordinary conditions of hydrothermal synthesis; hydrosilicate appears at atmospheric pressure and temperatures as low as 200° in the almost-dry catalyst.

TEJIMA, T. *See abs.* 1918, 1919, 1920, 1921, 1922, 1923, 1924, 1925, 1926.

TELEGIN, V. G. *See abs.* 2030, 2033, 2034.

3364. TELEGIN, V. G., AND Sidorov, N. V. [Utilization of Artificial Magnetite as a Raw Material for the Preparation of the Catalyst for Ammonia Synthesis.] *Jour. Appl. Chem.* (U. S. S. R.), vol. 11, 1938, pp. 1064-1070 (in French, p. 1070); *Chem. Abs.*, vol. 33, 1939, p. 4386.

Magnetite was prepared from commercial Fe (containing C, 0.12; Si, 0.09; and Mn, 0.05%) by oxidation with O₂ at 1,470°-1590°. The magnetite obtained was mixed with Al₂O₃ and KNO₃, and the mixture was used for the preparation of catalyst by electric fusion. The activity of the catalyst obtained was higher than that prepared from the concentrates of natural magnetite; this is explained by the small amount of SiO₂ in the artificial magnetite. The activity of catalyst prepared from an artificial magnetite, after heating at 625° for 8 hr. in the N₂-H₂ atm., was changed as follows: The activity corresponding to 400°, 450°, and 475° decreased, but that corresponding to 500° and 525° increased. 9 refs.

3365. — [Siderite as a Catalyst for Ammonia Synthesis.] *Jour. Appl. Chem.* (U. S. S. R.), vol. 12, 1939, pp. 1769-1774 (in French, p. 1774); *Chem. Abs.*, vol. 34, 1940, p. 8,188.

Bakal (Ural) siderite contained FeO, 38.50; Fe₂O₃, 1.60; Al₂O₃, 2.20; SiO₂, 2.80; MgO, 13.25; CaO, 0.92; CO, 38.70; As, none; P, 0.001; S, 0.12 (as sulfate), and H₂O, 1.15%. The synthesis of NH₃ was attempted at normal pressure and under 300 atm. The sample of siderite containing ferrous oxide was inactive at atmospheric pressure and only slightly active at 300 atm., while samples containing the catalyst in the form of ferric oxide were more active. The highest activity was reached with a catalyst containing the Fe in the form of Fe₂O₃. 15 refs.

3366. TELEGIN, V. G., SIDOROV, N. V., AND SHEPLENKO, K. B. [Effect of the Content of Aluminum Oxide in the Iron Catalyst for Synthesis of Ammonia Upon Its Activity at Atmospheric Pressure.] *Jour. Appl. Chem.* (U. S. S. R.), vol. 13, 1940, pp. 823-830 (in French, p. 830); *Chem. Abs.*, vol. 35, 1941, p. 2257.

Chemical compositions of NH₃ catalysts were FeO, Fe₂O₃, Al₂O₃, and K₂O, respectively, (1) 32.05, 64.40, 3.55, and 0%; (2) 27.75, 63.00, 9.25, and 0%; (3) 25.15, 46.60, 28.25, and 0%; (4) 13.40, 23.50, 61.10, and 0%; (5) 20.40, 71.10, 5.20, and 2.94%; (6) 20.30, 52.70, 25.00, and 2.50%; and (7) 14.50, 43.60, 39.60, 2.10%. The catalysts were prepared by fusion of magnetite with Al₂O₃ and with Al₂O₃ and KNO₃ in the electric furnace. The activity of catalysts was determined at a volume velocity of N₂-H₂ gas mixture of 15,000 l. per hr. per l. of catalyst at 310°-500°; for the last 3 catalysts also at a volume velocity of gas mixture of 2,000, 5,000, and 10,000. In all cases, activity decreased with an increase of Al₂O₃ content. A minimum amount of Al₂O₃ necessary for the stabilization of microstructure and activity of reduced Fe in the NH₃ catalyst should be determined by the working conditions. Thus, if a catalyst containing 0.1% Al₂O₃ is stable enough at a

temperature below 450° at atmospheric pressure; then for stable activity at 500° and 300 atm. the catalyst should have up to 5% Al₂O₃. The binary catalysts (Fe-Al oxides) were more active than ternary catalysts (Fe-Al-K oxides), probably because of the poisonous effect of K₂O.

TELLEB, E. *See abs.* 389, 2230.

TEMKIN, M. *See abs.* 1773.

3367. TEMKIN, M., AND KIPERMAN, S. [Kinetics of Synthesis and Decomposition of Ammonia on Various Catalysts.] *Jour. Phys. Chem.* (U. S. S. R.) (in Russian), vol. 21, 1947, pp. 927-952; *Chem. Abs.*, vol. 42, 1948, p. 2501.

Equation for the rate v of reaction, $v=k_1P_1(P_2^2/P_3^2) - k_2(P_3^2)^{1-\alpha}$, in which P_1 , P_2 , and P_3 are the partial pressures of N₂, H₂, and NH₃, respectively, and k_1 , k_2 , and α are constant, is integrated by assuming the total pressure to be constant. The energy of activation is expressed as a function of α . The best composition of the gas mixture is given by $P_2:P_1=3\alpha$. The above equation is valid only when the system is not too far removed from the equilibrium state. Variations of the adsorbed amount of N₂ may cause the decomposition of NH₃ to be a zero-order reaction at very low NH₃ concentrations. Consideration of earlier experiments shows that the equation is valid for various catalysts (Fe, Mo, W, U, Ce, Mn, Os, Ru, Cu, and Pt), that a usually is 0.5, and that the activation energy is almost independent of the nature of the catalyst. This proves that the reaction mechanism is identical on various catalysts. The rate of synthesis should depend on the degree of uniformity of the catalyst surface. 57 refs.

3368. TEMKIN, M., AND PYZHEV, V. [Kinetics of the Synthesis of Ammonia on Promoted Iron Catalysts.] *Jour. Phys. Chem.* (U. S. S. R.), vol. 13, 1939, pp. 851-867; *Chem. Abs.*, vol. 34, 1940, p. 6512.

From experimental data on the synthesis and decomposition of NH₃ technical Fe catalysts promoted by Al₂O₃ and K₂O at 400°-450° and 1 atm. pressure and H₂:N₂ ratios of 0.5 up to 8.5, the rate constants are $k=1.04 \times 10^4$ at 400° and 7.78 at 450°. The rate of formation of NH₃ is given by $v=k_1P_{N_2}(P_{H_2}^2/P_{NH_3}^2)^\alpha$ with $\alpha=0.5$. The determining factor in the forward process is the rate of activated adsorption on the N₂-free surface. For the reverse process, the rate of NH₃ desorption is the rate-determining factor. For the complete process, the equation

$$dP_{NH_3}/dt = k_1(P_{N_2}P_{H_2}^2/P_{NH_3}) - k_2(P_{NH_3}/P^{1-\alpha})$$

holds both for the experimental data of Temkin and Pyzhev and for those of other authors. The apparent energy of activation for NH₃ formation is ~14 cal. and for decomposition ~40 cal. per mol.

3369. TEMKIN, M. I., KIPERMAN, S., AND LUK'YANOVA, L. I. [Flow-Circulation Method of Investigation of the Kinetics of Heterogeneous Catalytic Reactions.] *Doklady Akad. Nauk. S. S. R.*, vol. 74, 1950, pp. 763-766; *Chem. Abs.*, vol. 45, 1951, p. 1854.

This is an adaptation of the idea of Denbigh, subsequently utilized by Hammett for homogeneous reactions. The reacting gas is admitted to the catalyst zone at a constant velocity v , is made to circulate through the reaction zone, and is led out at exactly the velocity v . Provided the velocity of the circulation through the reaction zone is very much greater than the velocity v of inflow and outflow, the variation of the composition of the reacting gas in each single pass is negligible, and that composition can be taken as stationary. A check is provided by splitting the outgoing gas stream into 2 portions led out of the system just before and after the catalyst zone, with the sum of the 2 outgoing gas streams equal to v ; fulfillment of the constancy of composition in each single pass is indicated by closeness of the compositions in the 2 branches

of the outgoing gas. The method was applied to the synthesis of NH_3 from a stoichiometric N_2+3H_2 gas mixture on 1 cc. of a synthetic NH_3 catalyst at 451° , with rates of circulation of 360–500 l. gas per hr., and v varies between about 9 and 110 l. gas (STP) per hr. With U =volume of gas flowing in and out per unit time, c =concentration of the product in the total outgoing gas, W =volume of the catalyst, f =free fraction of the catalyst volume. The rate k of the reaction can be expressed by cU/fW , or in terms of the partial pressure p_A' of NH_3 in the initial gas mixture, $p_A'U/fW$, or, on account of the insignificant volume change, $r=p_A'U/fW$, where p_A' =partial pressure of NH_3 in the outgoing gas. The previously established Temkin (abs. 3367) kinetic law for the catalytic synthesis of NH_3 , $r=k_1 p_{\text{H}_2}^{0.5} p_{\text{N}_2}^{0.5} / (1 + k_2 p_{\text{H}_2}^{0.5} + k_3 p_{\text{N}_2}^{0.5})$ (with the exponent 0.5 valid for the particular catalyst), gives $k = \gamma^2 p_{\text{H}_2}^{0.5} p_{\text{N}_2}^{0.5} (U_0/W) / (1 - \alpha^2)$, where $\gamma = p_{\text{H}_2}^{0.5} p_{\text{N}_2}^{0.5} p_A'$; P =total pressure; $U_0=U$ reduced to 0° and 1 atm.; $k = 273f/k_2 0.73^{1.5} P_0 T$ ($P_0=1$ atm.); α =yield of NH_3 in fractions of the equilibrium NH_3 content ($\approx 0.210\%$). Experimental data ($U_0/W=8960, 20,000, 46,900, 69,800, 86,200, 110,000$ ml. gas (STP) per ml. catalyst per hr., $\alpha=0.726, 0.603, 0.461, 0.388, 0.355, 0.302$) give k (av.) $\approx 12 \times 10^3$, fairly close to the previously determined $k=7.8 \times 10^3$ by the simple flow method.

3370. TENENBAUM, M., AND JOSEPH, T. L. Reduction of Iron Ores Under Pressure by Carbon Monoxide. Am. Inst. Min. and Met. Eng., Tech. Pub. 1134, 1939, 18 pp.; Chem. Abs., vol. 34, 1940, p. 2752.

Most rapid rate of reduction was obtained with H_2 . Rate was increased 40% by doubling pressure. With pure CO , the rate was about $\frac{1}{4}$ that with pure H_2 . Doubling the pressure increased rate of reduction by 23%. Dilution of CO with N_2 to form bosh gas lowered reduction rate by $\frac{1}{2}$. Doubling the pressure increased the rate about 20%. Substitution of 3.2% CO_2 for an amount of CO in bosh gas reduced rate still further. Pressure is most effective when applied to strongly reducing gases, rather than to those approaching equilibrium composition. Theoretical considerations are discussed.

TENNEY, R. F. See abs. 155, 156.

TENTSCHART, H. See abs. 1948.

TERASAKI, Y. See abs. 3174.

3371. TEMINASOV, Y. S., AND BELETSKI, M. S. [X-Ray Investigation of the Structure of the Nickel Skeleton Catalyst.] Doklady Akad. Nauk S. S. R., vol. 63, 1948, pp. 411–413; Chem. Abs., vol. 44, 1950, p. 9784.

Catalyst obtained after leaching out the Ni_2Al with alkali and subsequent self ignition of the Ni residue consists of a mixture of cubic Ni (lattice constant $a=3.52$ Å) and NiO ($a=4.15$ Å). If, after leaching, the catalyst is stored under H_2O to prevent oxidation, X-ray patterns reveal hexagonal Ni, with $a=2.56$, $c=4.16$ Å. These lattice constants are distinctly lower than those of the hexagonal Ni of Bredig and Alolio (abs. 337), evidently as a result of occlusion of H_2 in leaching. The grain size of the hexagonal Ni in the skeleton catalyst is of the order of 10^{-3} – 10^{-4} cm. Self ignition and the accompanying heating-up evidently result in a conversion of the hexagonal Ni into cubic Ni.

TER-NEDDEN, W. See abs. 1047.

3372. TERNISEN, J. [Catalytic Oxidation and Influence of Catalyst Surface.] Chim. et ind., vol. 58, 1947, pp. 234–237.

Because of the ease with which H_2 is more or less adsorbed between 300° and 700°C , it was used in the study of surface. Adsorption by catalyst, with or without support is compared. Calculation using the Brunauer-Emmett-Teller equation showed the supported catalyst to be far superior to the unsupported.

The active surface of the supported catalyst lost 5% of its efficiency at 500°C , 26% at 600° and 75% at 650° . After several hours use at the last temperature it lost 39%. The dimensions of surface for the same quantity of metal catalyst deposited are determined by comparing them to a standard surface magnified and photographed by the electron microscope.

3373. TERRES, E., AND PONGRACZ, A. [Reactions in the Blast-Furnace Equilibrium.] Ztschr. Elektrochem., vol. 25, 1919, pp. 386–407; Chem. Abs., vol. 14, 1920, p. 919.

Reversible reaction represented by the equation $\text{Fe} + \text{CO}_2 = \text{FeO} + \text{CO}$ has been studied and the equilibrium ratio of the gases determined at temperatures 550° – 950° by approaching the equilibrium from both sides and varying the quantities of the starting materials. On plotting the ratio of the initial gas concentration, CO_2 or CO , to the equilibrium concentration of the mixed gases, $\text{CO}_2 + \text{CO}$, at equilibrium against the equilibrium temperature, a curve is obtained, which, in agreement with the results of Schenck and his co-workers and in disagreement with those of Baur and Glaessner, shows no minimum and is almost linear. It has been found that the quantity of Fe exerts an influence on the system, the position of equilibrium being displaced so as to favor the formation of CO as the amount of metal is increased. An analytical method and special apparatus have been developed for determining quantitatively in a mixture the amounts of Fe in the different states of oxidation. The action of CO_2 on Fe in a closed vessel results in the formation of both FeO and Fe_3O_4 , from which the existence of solid solution is deduced by means of the phase rule. In conclusion, it is shown that at higher temperatures Fe can probably absorb considerable quantities of CO_2 and CO .

3374. TERRES, E., PATSCHEKE, G., HOFMANN, H., KOVACS, S., AND LÖHR, O. [Formation of Water Gas and the Behavior of Brown-Coal and Bituminous-Coal Cokes and Semicokes in Water-Gas Generation.] Gas u. Wasserfach, vol. 77, 1934, pp. 585–587, 628–636, 650–653, 666–669, 681–684, 703–706; Chem. Abs., vol. 29, 1935, p. 577.

Cokes and semicokes from the bituminous coal Unser Fritz and from several brown coals were prepared at various temperatures 300° – $1,200^\circ$ and gasified at slightly lower temperatures in N_2 -containing H_2O vapor. Merck wood charcoal also was gasified. The water-gas analyses were used to calculate the extent of steam decomposition, $\text{CO}:\text{CO}_2$ ratios, and the water gas and Boudouard equilibrium; similar calculations were made for the theoretical steam-C equilibrium at temperatures 400° – $1,200^\circ$ with the N_2 0–100% saturated with H_2O . At $1,200^\circ$, the bituminous coal coke gave a steam decomposition, $\text{CO}:\text{CO}_2$ ratios, and the C gasification distinctly lower than the corresponding equilibrium values, and lower than wood charcoal. The reactivity of the bituminous-coal cokes decreased with increasing carbonizing temperatures. The brown-coal cokes and semicokes reached no consistent gasification equilibrium. Steam decomposition increased with increasing gasification temperature and with decreasing saturation and lower rate of flow of the gasifying medium. The reactivity with steam of the carbonized product increased with carbonizing temperature up to 700° , decreasing at higher temperatures. This is attributed to a progressive uncovering of the C structure at the lower temperatures followed by the production of a coarser structure at higher temperatures. Steam decomposition is initially, more or less proportional to the time of contact, then increases more or less rapidly according to the reactivity of the material, and then at a lower rate, probably without reaching an equilibrium value in a reasonable time. Carbonized materials can be arranged in the following order with

respect to increasing water gas formation and increasing reactivity: Graphite, lamp black, bituminous-coal coke and semicokes, wood charcoal, and brown-coal cokes and semicokes. The water gas equilibrium was approached in the gasification of the wood charcoal and bituminous-coal cokes at about 600° and attained above 750° . This equilibrium was obtained slowly in an empty porcelain tube at 600° . The brown-coal cokes and semicokes showed no regularity in attaining this equilibrium. The Boudouard equilibrium $\text{C} + \text{CO}_2 = 2\text{CO}$ was not fulfilled in any of these experiments. By using the Ostwald gasification triangle, it was shown that the reaction of steam with bituminous-coal coke and wood charcoal was free from secondary reactions, but that the brown-coal semicokes results showed an excessive and unexplained O_2 action. The use of the gasification triangle showed that the results of Harries and of Gwosdz with wood charcoal and coke were free from secondary reaction effects, but that the results of Bunte and Glissen (abs. 407), on various cokes showed a surprising excess of H_2 . An attempt was made to correlate surface activity, as determined by the heat of wetting of several brown-coal cokes and semicokes, with reactivity, but there appeared to be no distinct relationship. The influence of carbonizing temperature, gasification temperature, steam content, and time of contact of the gasifying medium on the gasification of the coke S content was investigated. Various views as to the nature of the primary action of steam on C are contrasted. When the reaction of steam with carbonized materials does not follow the water gas equilibrium, the principal reaction is believed to be largely, if not entirely, $\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$, as larger amounts of CO are formed than can be accounted for by the water gas equilibrium. 57 refs.

3375. TERWEN, J. W. [Contribution to the Theory of the Water-Gas Process.] Chem. Weekblad, vol. 19, 1922, pp. 400–401; Chem. Abs., vol. 17, 1923, p. 1542.

Among some errors in the work of Kohn (abs. 1938) the chief is the assertion that in the 2 equations, $\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$ and $\text{CO} + \text{C} = 2\text{CO}$, the fraction of steam transformed according to the 1st equation should be equal to the quantity of CO_2 that disappears according to the 2d equation.

3376. ———. [Adsorption of Hydrogen by Nickel.] Chem. Weekblad, vol. 21, 1924, pp. 386–389; Chem. Abs., vol. 18, 1924, p. 3507.

Gauger and Taylor found that the amount of H_2 adsorbed by Ni decreases with rising temperature. This is explained by assuming that H_2 molecules as well as H atoms are bound by the Ni atoms and that for every temperature a dynamical equilibrium between both forms is established. A typical $T-\alpha$ curve for this equilibrium can be drawn from Gauger and Taylor's data, showing that at the higher temperatures the adsorbed quantity of H_2 approaches asymptotically half the amount of H_2 adsorbed at the lowest temperature.

3377. TESTER, R. [Chromium Carbides.] Compt. rend., vol. 203, 1936, pp. 1007–1009; Chem. Abs., vol. 31, 1937, p. 332.

Powdered Cr and excess C heated in an electric furnace above $1,700^\circ$ form Cr_3C_2 , which is not attacked by O_2 below $1,000^\circ$, and so is separated from excess by heating in O_2 at 900° . It is insoluble in hot concentrated HCl , and is slowly volatile above $1,900^\circ$. Between $1,500^\circ$ and $1,700^\circ$ Cr_3C_2 is formed with some Cr_2C_3 ; this is less as temperature is nearer $1,500^\circ$. Cr_3C_2 is soluble in concentrated HCl but not in the 10% acid; it also is not attacked by O_2 below $1,000^\circ$. Below $1,400^\circ$ some Cr_2O_3 is formed. Cr_2C_3 also is formed by heating Cr in C_2H_2 . CO passed over Cr at the temperature above $1,350^\circ$ reacts according to $19\text{Cr} + 6\text{CO} \rightarrow 3\text{Cr}_3\text{C}_2 + 2\text{Cr}_2\text{O}_3$, the rate rapidly increasing with temperature. Below $1,350^\circ$ some C also is formed.

3378. THAU, A. [Large-Scale Low-Temperature Carbonization and Production of a Gas Mixture for Synthesis of Fuels.] Oel u. Kohle Erdöl Teer, vol. 11, 1935, pp. 815–822; Brennstoff-u. Wärmewirt., vol. 17, 1935, pp. 167–176; Chem. Abs., vol. 30, 1936, p. 3969.

Various phases of operation are discussed in describing the Lurgi, Didier, and Fischer-Tropsch processes.

3379. ———. Motor Spirit From Coke. Colliery Guard., vol. 150, 1935, pp. 335–337; Chem. Zentralb., 1936, II, p. 785.

Lengthy abstract of an article by Fischer (abs. 962).

3380. ———. Synthetic Motor Spirit. Coal Carbonisation, vol. 2, 1936, pp. 159–163; Chem. Abs., vol. 30, 1936, p. 7815.

It is uneconomical to produce less than 20,000 tons of gasoline per yr. The whole production of coke and coke-oven gas can be converted into a gas suitable for synthesis of gasoline. Current processes, especially those used in Germany, are described in detail with drawings and plant photographs.

3381. ———. [Gasoline and Oil Synthesis From Water Gas.] Gas-u. Wasserfach, vol. 80, 1937, pp. 911–913.

Brief descriptions of the Schmalfeldt-Wintershall process for making synthesis gas from raw brown coal, and its application to the Fischer-Tropsch synthesis of gasoline and oil. A flow diagram and a heat chart of the latter.

3382. ———. [German Coals as a Starting Material for Refined Chemicals.] Brennstoff-u. Wärmewirt., vol. 19, 1937, pp. 17–25, 41–45; Chem. Abs., vol. 31, 1937, p. 4084.

Review of methods for converting coals to liquid hydrocarbons.

3383. ———. [Synthesis of Benzine by the Bindley Process.] Oel u. Kohle, vol. 13, 1937, pp. 350–353; British Chem. Abs., 1937, B, p. 750.

S content of the initial gas is reduced to 0.002 gm. per m^3 by 1st removing the H_2S over Fe oxide, hydrogenating the organic S compounds over a $\text{CuO}-\text{PbCrO}_4$ catalyst, and finally removing the H_2S so produced by means of Fe oxide, followed by washing with aqueous $\text{K}_2\text{Fe}(\text{CN})_6$. The synthesis itself is carried out at 200° per atm. in presence of a Ni-Mn- Al_2O_3 -Kieselguhr catalyst. The latter is agglomerated by mixing it with Et orthosilicate and exposing it to moist air before reduction. Ordinary water gas (CO , 42; H_2 , 48%) may be used as the initial gas. The process is preferably carried out in stages, the hydrocarbons formed being removed after each stage. The course of the reaction may be represented by $\text{CO} + 1.5\text{H}_2 = (\text{CH}_2)_n + 0.5\text{H}_2\text{O}$.

3384. ———. [Oil Production From Coal. Its Technical and Economical Valuation From an Australian Viewpoint.] Brennstoff-u. Wärmewirt., vol. 20, 1938, pp. 87–92; Chem. Abs., vol. 32, 1938, p. 6835.

Discussion of the economics of coking, hydrogenation, and benzene synthesis.

3385. ———. [Treatment of Coal for the Production of Power Materials.] Ztschr. Ver. deut. Ing., vol. 82, 1938, pp. 129–133; Coal Carbonisation, vol. 4, 1938, p. 64; Chem. Abs., vol. 32, 1938, p. 3124.

Review of all the principal methods of coal processing for the production of fuels from coal. The methods that have been developed for the low-temperature carbonization of hard coals and brown coal are enumerated, and descriptions are given of the Lurgi internally heated ovens and the Borsig-Geissen rotary alloy-steel retorts. Particulars are given of the Bubiag-Didier, Koppers, Wintershall-Schmalfeldt, Pintsch-Hillebrand, Lurgi, Schmidt and Groh, and Demag gasification processes for the production of synthesis gas. Processes for the synthesis of motor fuels by hydrogenation vary according to whether the hydrocarbon is treated in the

gaseous, liquid, or solid phase. All the chief processes are described with flow diagrams and representative data. The paper concludes with notes on the processing of tar, the economics of the manufacture of motor fuels from coal, and a bibliography of 28 refs.

3386. [Synthesis of Hydrocarbons From Water Gas.] Ztschr. Ver. deut. Ing., vol. 83, 1939, p. 906. Review.

3387. [Water-Gas Production With External Heating.] Gas- u. Wasserfach, vol. 84, 1941, pp. 509-513; Chem. Abs., vol. 36, 1942, p. 5334.

Water-gas reaction, being endothermic, requires a continuous supply of heat if it is to be maintained as a continuous process. Heat can be supplied in various ways, for example, continuous supply of O_2 in place of air, direct supply of superheated steam, and external heating of the generator. Processes involving an externally heated generator, for example, those of Heller, Herzberg and Bueb, are reviewed. The Didier-Bubiag process, in which an externally heated and continuous vertical retort is used, is described. In this the gas outlet is moved from the top of the retort to about halfway down. The raw, weakly or noncoking, coal before entering the retort passes through a drying chamber, which can also be adapted to submit the coal to a preliminary low-temperature carbonization. Superheated steam is introduced toward the bottom of the retort, the lowest section of which is not heated and serves to cool the issuing coke. The coal in passing down the retort is progressively carbonized in the zone above the gas outlet, and the carbonization gases must pass downward to reach the outlet; in doing so the tarry vapors are cracked. Water gas is produced in the lower half of the retort and passes upward to the same gas outlet. The operation is adjusted so that just enough coke leaves the retort to supply producer gas for external heating. Conditions can be varied to yield either a rich gas or synthesis gas. If lignite briquets are used, subjected to low-temperature carbonization in the pretreatment chamber, and the tarry vapors are led down through the top of the retort, C_6H_6 containing 18-25% of toluene can be recovered.

3388. [Large-Scale Water-Gas Production for Chemical Synthesis.] Oel u. Kohle, vol. 38, 1942, pp. 589-601, 617-624, 685-690, 721-727, 749-765; Gas Times, vol. 44, 1945, p. 32; Gas Abs., Inst. Gas Technol., vol. 1, No. 7, 1945, p. 12.

For the manufacture of NH_3 , a synthesis gas containing H_2 and N_2 in the ratio 3 : 1 is required, while, for the production of MeOH and liquid fuels, a gas consisting of H_2 and CO in the ratio 2 : 1 is required. The production of synthesis gas of such required compositions has been achieved in Germany by 5 distinct systems of gasification processes. The method of supplying the required heat for the endothermic decomposition of steam by C has been chosen by the author as the basis of classification. (1) In the 1st class belong the gas generators, employing coke or brown coal as fuel, which operate with intermittent blast and make cycles, such as those built by the Bamag and Viag concerns. The Viag generators, however, combine this method of heating with the principle of recirculation. (2) The 2d group comprises those processes that employ O_2 for the internal supply of heat, which makes the operation continuous. The Winkler, Lurgi, and Thyssen-Galocsy processes belong in this class. (3) Among the processes using indirect heat transfer by recycling part of the produced gases that had been preheated to the required high temperature in intermittently operated regenerators, belong the Pintsch-Hillebrand, Koppers, and Wintershall-Schmalfeldt processes. (4) A group employing direct heat transfer by external heating con-

prises the Bubiag-Didier, Reiche Zeche, and Ahrens processes, although in the latter the principle of heat transfer by recirculation is combined with external heating. (5) The last class includes all other methods of heat transfer employed, such as heating of the reaction chamber by means of electricity as in the Hote and Stassano processes, the use of highly superheated steam in the Pattenhausen process, the use of molten salt bath proposed by Lichtenberger and Haiser. The gas produced by some of these methods needs further processing with steam, either to convert the excess CO into H_2 , $CO + H_2O \rightarrow H_2 + CO_2$, or to decompose the CH_4 into CO and H_2 , as is done in the Wild, Gesent, Bamag, and Viag processes by means of a catalyst employed, which also removes the organic S compounds. In the Kuhlman, Linde, and Padovani processes, the same end is achieved by hot surfaces. For the removal of the excess CO, the alkali process, pressure washing with water, or other processes have been used.

THENARD, A. See abs. 3389.

3383. THENARD, P., AND THENARD, A. [Effect of Electricity on Mixtures of Marsh Gas and Carbon Dioxide and of Hydrogen and Carbon Monoxide.] Compt. rend., vol. 76, 1872, pp. 1049-1051; Jour. Chem. Soc., 1873, p. 364; Chem. Zentralb., 1873, p. 452.

In performing the same experiments as Brodie on the conversion of $CO + H_2$ by the electric current, it was found that the reaction goes farther than the production of CH_4 and that liquids of complex composition are obtained. Berthelot considers that they result from the condensation of OH_2O , which is the 1st product of the reaction between CO and H_2 .

THIBLE, E. W. See abs. 1366.

3390. THIESSEN, G. Bituminous Coal. A Source of Gaseous and Liquid Fuels. Chem. Inds., vol. 38, 1936, pp. 340-353; Chem. Zentralb., 1936, II, p. 565; Chem. Abs., vol. 30, 1936, p. 3965.

Review of carbonization, high-pressure hydrogenation, and synthesis from CO and H_2 .

TRODOS, G. See abs. 1959.

THOMAS, B. See abs. 3556.

3391. THOMAS, B. W., AND SEYFRIED, W. D. Mass-Spectrometer Analyses of Oxygenated Compounds. Anal. Chem., vol. 21, No. 9, 1949, pp. 1022-1026.

By means of special techniques, mass spectrometric methods have been developed for the quantitative determination of individual oxygenated compounds containing 5 or less C atoms per mol. In mixtures containing 6 or less components the average accuracy is better than $\pm 1\%$ based on the total sample; for more complex mixtures, the accuracy is in the order of $\pm 2\%$ or less. H_2O in moderate concentrations has a negligible effect on the accuracy of the oxygenated compound determinations, and H_2O is determined with an average deviation of $\pm 1\%$. A complete analysis of a 6-component mixture can be performed in about 2 hr., and only a few drops of sample are needed. Calibration data for 10 alcohols, 3 ketones, 6 aldehydes, 3 esters, 4 acids, and 2 ethers are presented.

3392. THOMAS, P. R., DOWN, L., AND LEVIN, H. Determination of Carbon Monoxide in Hydrocarbon Gases Containing Olefins. Anal. Chem., vol. 21, No. 12, 1949, pp. 1476-1480.

Studies of hydrocarbon synthesis and catalytic cracking make it necessary to determine CO in gases containing large amounts of olefins. All hydrocarbons except CH_4 are removed rapidly by condensation in liquid N_2 from which the uncondensed gases—CO, H_2 , N_2 , O_2 , and CH_4 —are removed by Toepfer pump. Orsat apparatus is used to remove O_2 from this mixture and to determine CO. The major part of the CO is absorbed in acid cuprous chloride and the remainder in cuprous sulfate-2-naphthol. CO is determined in con-

centrations from 0.1-100% with an average error of less than 0.5% of the CO in the samples containing 10% CO. The accuracy is somewhat less for lower concentrations. The total time required for the determination is less than 1 hr.

THOMAS, R. W. See abs. 2489.

THOMAS, V. See abs. 299, 300.

3393. THOMAS, W. H., AND FARAGHER, W. F. Interrogation of Dr. C. H. N. Benschmann. BIOS Final Rept. 597, 4 pp.; PB 44,946.

In October 1945, an account was made of contacts with The Texas Co. and the events leading up to the appointment of the company as agent for the Fischer-Tropsch process in the United States.

THOMPSON, J. K. See abs. 1418.

3394. THOMPSON, M. DEK. Specific-Heat Equations for Carbon Dioxide, Carbon Monoxide, Steam, Hydrogen and Oxygen, and the Free-Energy Equation for the Water-Gas Reaction. Trans. Electrochem. Soc., vol. 82, 1942, pp. 397-402; Chem. Abs., vol. 36, 1942, p. 6385.

Least-square solutions for the specific-heat equations of the above gases are worked out for the forms $C(p) = a + bT + cT^2$, $C(p) = a + bT + cT^2$, and $C(p) = a + bT + cT^{-1/2}$, and the sums of the squares of the deviations of $C(p)$, $\Sigma \text{dev.}^2$, calculated by each equation, from the experimental values are compared. The equation giving the smallest $\Sigma \text{dev.}^2$ being the best, it is found that, for the temperature range 300°-3,000° or 3,500° K., the T^2 equation is the best for CO and steam, the $T^{-1/2}$ equation is the best for H_2 , and the T^2 equation is the best for CO_2 and for O_2 . The equation for ΔG° of the water-gas reaction is then computed, and the values of $\log K$ computed by this equation are compared with the values obtained directly from spectroscopic observations.

THOMPSON, O. F. See abs. 451, 452, 453.

3395. THOMPSON, S. O., TURKOVICH, J. AND IRSA, A. P. Reaction of Deuterium With Hydrocarbons Over a Cobalt-Thoria Fischer-Tropsch Catalyst. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 5213-5215.

H exchange reactions were observed between D_2 and C_2H_6 , C_2H_4 , C_2H_2 , and iso- C_3H_8 , when a mixture of 6 vol. of D_2 and 1 vol. of each of the hydrocarbons was passed over a Fischer-Tropsch CO catalyst under conditions of temperature and flow rate similar to those for hydrocarbon synthesis. The exchanged products were found to be extremely deuterated and the mole % of hydrocarbon molecules undergoing exchange was < 10% in the case of the ethanes and propanes, 45% for n-butane and 51% for isobutane. Cracking of the hydrocarbon gases to produce deuterated CH_4 was also observed. The exchange reaction of CH_4 and D_2 and CD_4 and CH_4 was also studied.

3395a. Study of the Fischer-Tropsch Reaction Using Deuterium Gas. Jour. Phys. Chem., vol. 56, 1952, pp. 243-250.

Description is given of an apparatus for the production of deuterocarbons from deuterium and CO. The various deuterocarbons and waxes are examined for their mass spectrum patterns and infrared spectra.

3396. THOMPSON, G. H. Hydrocarbon Synthesis. British Coal Utilisation Research Assoc. Bull., vol. 8, 1944, pp. 191-201; Chem. Abs., vol. 38, 1944, p. 6513.

Work is reviewed on the Fischer-Tropsch synthesis and the preparation and properties of the secondary products, motor spirit, diesel oil, lubricating oils, and paraffin wax. 111 refs.

3397. THOMPSON, G. H., AND GIVEN, P. H. Hydrocarbon Synthesis. Butterworth's Sci. Publication, "Progress in Coal Science", London, 1950, pp. 332-352; Fuel Abs., vol. 8, No. 6, 1950, abs. 4602.

Synthesis processes for production of motor fuel and aliphatic compounds for the chemical industry are reviewed. Production of synthesis gas and S removal; catalysts, their life, regeneration, and recovery; plant design and operation; primary products; and effect of pressure and other operating variables are outlined. Secondary products include high-grade motor fuel, lubricants, synthetic soaps and edible fats, sulfate detergents, and alcohols. Related processes described include isosynthesis, Oxo synthesis, use of Ru catalysts, and oxidation of hard wax. Theories of catalyst structure and reaction mechanism are given. Recent developments include the modified Fischer-Tropsch process, use of fluidized bed, Fe catalysts, and lower H_2 :CO ratios giving modified products. All these plus cheaper synthesis gas production are necessary before the process can become a commercial proposition.

3398. THONON, C., AND JUNGERS, J. C. [Dehydrogenation of Secondary Alcohols in the Liquid Phase With Nickel as a Catalyst.] Bull. soc. chim. Belg., vol. 58, 1949, pp. 331-349; Chem. Abs., vol. 44, 1950, p. 3876.

Ketone produced during the dehydrogenation of secondary alcohols has a strong inhibitory action on the further reaction. It has a markedly higher adsorption coefficient than the alcohol. The factors influencing the ratio of the adsorption coefficients of the ketone and alcohol are examined; for example, the temperature, the solvent, and the catalyst. 2-Propanol and 2-butanol are dehydrogenated under various conditions. The temperature increases the rate of reaction and changes the ratio in favor of the alcohol. No obvious influence of the solvent on the ratio has been observed. Different samples of Ni and Cu are used as catalysts. Cu is less active than Ni, but it changes the ratio slightly in favor of the alcohol.

3399. THOREN, F. [Activity and Temperature Relationships for Nickel Catalysts. I.] Ztschr. anorg. Chem., vol. 163, 1927, pp. 367-395; Chem. Abs., vol. 21, 1927, p. 3804.

Activities of Ni catalysts prepared in various ways were measured by a static method. The reactions used were: $C_2H_4 + H_2 \rightarrow C_2H_6$; $C_2H_4 + 3H_2 \rightarrow C_2H_6$; $O_2 + 2H_2 \rightarrow 2H_2O$. The activity of the catalysts increased stepwise with increase in temperature. The mean values for the temperatures at which marked increase in activity was evidenced were 0.7°, 40.1°, 60.2°, 80.7°, 100.3°, 119.4°, 134.7°, 170.0°. The actual % increase in activity at the various activation temperatures was not reproducible. The activation temperatures were almost the same for all reactions and for different Ni catalysts. The activation of the H_2 is considered to be the cause of the phenomenon.

3400. [Activity and Temperature Relationships for Nickel Catalysts. II.] Ztschr. anorg. Chem., vol. 165, 1927, pp. 171-191; Chem. Abs., vol. 21, 1927, p. 3804.

Previously reported experiments on the hydration of C_2H_4 , C_2H_6 , and O_2 using the static method, indicated a stepwise increase in activity of Ni catalysts with increase in temperature. Further experiments on the hydration of C_2H_4 , using the dynamic method and a single catalyst, confirmed the earlier results. The average temperatures at which the irregular increases in activity occurred, appeared to be -18°, 41°, 61°, 81°, 100°, 120°, 139°, and 163°. The results were not reproducible with different samples of the same catalyst.

3401. THORNTON, D. P. Petrochemical Industry in the Southwest Builds for Growing Peacetime Markets. Nat. Petrol. News, Tech. Sec., vol. 38, No. 1, 1946, pp. R3-RS.

Among the many plants mentioned as producing and preparing to produce chemicals from petroleum is

Carthage Hydrocol, Inc., owned by several oil companies and Hydrocarbon Research, Inc., which is planning the construction and operation of a \$15,000,000 Fischer-Tropsch plant in the Panola gas fields of Panola Co., east Texas. It is reported that this plant will produce 5,000 bbl. per day of +80 octane gasoline, 1,000 bbl. per day of diesel fuel, and 200,000 lb. per day of crude alcohols (MeOH and EtOH) and acetone. It is stated that gasoline can be made for \$0.05 per 1,000 cu. ft. gas in competition with conventionally produced gasoline from \$1.00 crude. Study of the best features of the Fischer-Tropsch process in German plants plus research in this country will make this process competitive with conventional refinery production of gasoline. Byproducts can be converted relatively cheaply into chemicals and thus make Fischer-Tropsch gasoline and gas oils still more competitive with similar products from petroleum.

3402. ———. Japanese Research on Fuels. *Petrol. Processing*, vol. 2, No. 11, 1947, pp. 815-820.

Summary of the principal sources of fuels and lubricants and of the research work performed by the Japanese in obtaining supplies for war activities. The data are taken from the reports of the United States Naval Technical Mission to Japan. The peak year of the Seven-Year Plan to achieve a yearly production of about 1,000,000 kl. (6,300,000 bbl.) each of synthetic gasoline and fuel oil by 1943 occurred in 1944 when 114,000 kl. were produced, divided as follows: Hydrogenation 700 kl., Fischer-Tropsch 17,800 kl., low-temperature carbonization 95,400 kl.

3403. ———. Higher Propane Yields in Gasoline Plants by Hypersorption Process. *Petrol. Processing*, vol. 3, No. 11, 1948, pp. 1052-1054.

Summary of a paper by H. Kehde at the California Natural Gasoline Association meeting. Compare abs. 1070 and 1708. Basically the process depends on the adsorption of selected components of the gas by activated charcoal, 10-40 mesh, flowing continuously from the top of the hypersorption tower under controlled flow. The operation of a hypothetical plant is described. Investment and operating cost data for a plant recovering 98.5% propane are given. With a capital investment of \$542,000 and total operating expense, including amortization in 5 yr., of \$355,100, the cost per lb. of propane with a yearly production of 18.1 million gal. is \$0.0153. At a market value of \$0.068 per gal. for the propane, a payout time of 0.61 yr. before taxes is obtained.

See abs. 1207.

3404. THIRVE, M. W. Underground Gasification and British Coal Measures. *Inst. Fuel, Wartime Bull.*, February 1944, pp. 103-104; *Chem. Abs.*, vol. 38, 1944, p. 2471.

Review of recent Russian methods of underground gasification, including the chamber, sloping seam, gallery, and radial methods. The sloping seam method, applicable to seams inclined as much as 70°, appears most practical. Gas produced varies 115-210 B. t. u. and is said to contain, during the suction phase, H₂ and CO in the proper proportions for hydrocarbon synthesis.

TIBIRICA, J. See abs. 2240.

TIKHONOVA, Z. T. See abs. 1789.

3405. TIMASHER, A. S. [Reduction of Complex Chemical Compounds in Relation to Their Dissociation.] *Metallurg.*, vol. 14, 1939, No. 3, pp. 19-23; *Jour. Iron Steel Inst.* (London), vol. 140, 1939, A, p. 257.

Reduction of ferric, ferroso-ferric, and ferrous oxides with CO at 500° was studied in an apparatus in which a stream of CO was passed over the heated oxides, provision being made for continuous and automatic re-

duction of the temperature and the CO₂ content of the exit gases. Preliminary tests had shown that at the temperatures used, Fe had a negligible catalytic effect on the reaction 2 CO = CO₂ + C. The reduction of the ferric oxide took place in 2 stages, the 1st being irreversible and leading to the formation of 100% CO₂ (3 Fe₂O₃ + CO = 2 Fe₃O₄ + CO₂). The 2d stage corresponds to the reduction of the ferroso-ferric oxide with formation of a gas mixture of 47% CO₂ and 53% CO. The ferroso-ferric oxide is reduced directly to metallic Fe (Fe₃O₄ + 4 CO = 3 Fe + 4 CO₂). Under the experimental conditions the reduction of the ferrous oxide took place in 2 ways, namely, FeO + CO = Fe + CO₂ and by a complex reaction, the net result of which is represented by the reaction 4 FeO = Fe₃O₄ + Fe. The whole of the ferrous oxide is decomposed at the beginning of the reduction, which afterwards consists of the reduction of the ferrosoferric oxide.

3406. TRILL, T. [Liquid Fuels From Synthesis Gas.] *Tek. Tid.*, vol. 46, 1948, pp. 813-818; *Chem. Zentralb.*, No. 3, 1949, p. E234.

Review of the Fischer-Tropsch process for producing hydrocarbons from CO and H₂ and of the production of synthesis gas by the method developed in the United States by the oxidation of natural gas with O₂ under pressure. Natural gas preheated to about 650° is oxidized at 20 atm. and 1,300° according to the equation CH₄ + ½ O₂ = CO + 2H₂. The CO₂ formed is washed out and a part of the residual gas is converted at 300°-400° over Fe oxide into the desired ratio of CO:H₂. The synthesis itself is carried out at 17-35 atm. and about 300° in presence of finely pulverized Fe catalysts suspended in the synthesis gas and steam. From 3,000,000 m³ of natural gas there are produced daily 700 tons of gasoline (octane No. 80), 150 of light oil, and 130-160 of byproducts, such as alcohols, ketones, aldehydes, and carboxylic acids. The production cost per l. of liquid hydrocarbons is 5 öre, as compared with 19 by the German process. A simplified process for synthesis from coal is under development in the United States.

3407. TINGEX, H. C., AND HINSHELWOOD, C. N. Catalytic Decomposition of Formic Acid on Surfaces of Platinum and Silver. *Jour. Chem. Soc.*, vol. 121, 1922, pp. 1668-1676; *Chem. Abs.*, vol. 16, 1922, p. 4115.

TITZENTHALER, E. See abs. 1836, 2692.

3408. TIXIER, C. [Gasification and Application in the Chemical and Gas Industry.] *Jour. usines gaz*, vol. 73, 1949, pp. 186-189; *Chem. Zentralb.*, 1950, I, p. 472.

Basic equations for C gasification. Its application to the production of synthetic NH₃, the Bergius pressure hydrogenation, and the synthesis of oils and alcohols by the Fischer-Tropsch process is shown. The importance of gasification to modern processes for the production of high calorie gas is considered also.

TOJO, T. See abs. 1903.

TOMILOV, V. I. See abs. 2709.

TOMITA, N. See abs. 2514.

3409. TOMPKINS, F. C. Adsorption Isotherms for Nonuniform Surfaces. *Trans. Faraday Soc.*, vol. 46, 1950, pp. 580-586; *Chem. Abs.*, vol. 45, 1951, p. 18.

With certain restrictions regarding the magnitude of certain entropy changes, 4 well-known isotherms are deduced from variation of heat of adsorption with coverage. If the variation of net heat of adsorption with coverage is known either from theoretical calculations or experimentally from calorimetric measurements, the isotherm can be reasonably well characterized. If the concept of nonuniformity of surfaces is accepted, then the interpretation of transformations of state in adsorbed films on solids must be reconsidered.

3410. ———. Physical Adsorption on Nonuniform Surfaces. *Trans. Faraday Soc.*, vol. 46, 1950, pp. 569-580; *Chem. Abs.*, vol. 45, 1951, p. 18.

Nonuniformity of an adsorbent surface affects the isotherm obtained in physical adsorption both for localized and nonlocalized monolayers. Subject to the approximation that the internal partition function of the adsorbed molecule is independent of the adsorption potential of each site, it is shown that the log pressure versus log amount adsorbed is a linear plot, whether the adsorbed film is regarded as a polyphase or a monophase system.

See abs. 636.

3411. TONGUE, H. Design and Construction of High-Pressure Chemical Plant. Chapman & Hall, London, 1934, 420 pp.

3412. ———. Practical Manual of Chemical Engineering. D. Van Nostrand Co., New York, 1939, pp. 178-241.

Design and construction of pressure vessels for the chemical industry are included.

TOPLEY, B. See abs. 1422, 1423.

TOFF, N. E. See abs. 555.

3413. TORPOV, N. A., AND BORISENKO, A. I. [Solid Solutions in the System NiO-Fe₂O₃.] *Doklady Akad. Nauk. S. S. S. R.*, vol. 63, 1948, pp. 705-708; *Chem. Abs.*, vol. 43, 1949, p. 4552.

(1) Thermograms of NiO, show 3 endothermal effects, the 1st 2, at 180° and 340°, corresponding to loss of hygroscopic and crystal H₂O, respectively, the 3d, at 415°, to Ni₂O → 2 NiO + ½ O₂. On account of this dissociation, it is irrational to use Ni₂O to produce Ni ferrite. (2) Firing NiO + Fe₂O₃ mixtures prepared by drying the precipitated hydrates and pressing under 3,000 kg. per cm², at high temperatures is accompanied by deoxidation of the Fe₂O₃; thus, with the molecular ratios NiO:Fe₂O₃ = 2:3, 1:3, and 1:5, the amount of FeO after 3.5 hr. firing at 1,100°, 1,200°, 1,300°, 1,500°, was, respectively, 0, 0.70, 1.75, and 3.18; 0, 0.06, 2.67, 3.46; 0.08, 0.86, 4.32, 5.88%. (3) Products obtained by 40 hr. firing of NiO + Fe₂O₃ mixtures at 1,100° ± 10° showed, in petrographic examination, 1-phase structure only at the initial molecular ratios 1:1 and 2:3; at the latter ratio, crystallization of the ferrite is somewhat less distinct. With the molecular ratios 3:2, 2:1, and 3:1, product shows 2 phases, one of which is identified as Ni ferrite, the other NiO. Products of mixtures 1:2, 2:5, and 1:3 are equally 2-phase. (4) Debyeregrams show disappearance of the Fe₂O₃ lines in the 2:1 product, and also of NiO lines in the 1:1 and 2:3 products. Combination of the results shows that the 3:1, 2:1, and 3:2 products are mixtures of Ni ferrite and NiO, 3:1 is the pure ferrite, 2:3 is a solid solution of FeO in Ni ferrite, whereas, 1:2, 2:5, 1:3, and 1:4 are all mixtures of that solid solution and Fe₂O₃.

3414. TORPOV, N. A., PORAL-KOSHITS, E. A., AND BORISENKO, A. I. [Solid Solutions in the System CoO-Fe₂O₃.] *Doklady Akad. Nauk. S. S. S. R.*, vol. 66, 1949, pp. 905-908; *Chem. Abs.*, vol. 43, 1949, p. 7314.

In an equimolecular mixture of the precipitated hydroxides, ferritization is complete on 40 hr. heating at 1,100° of pellets dried at 120° and pressed under 3,000 kg. per cm². The thermal dissociation 6 Fe₂O₃ → 4 Fe₃O₄ + O₂, in mixtures with CoO, is less intense than in mixtures with NiO. In the presence of excess CoO, the product obtained is porous, and contains, on microscopic examination, 2 phases, 1 dark gray, the other dark yellow. The amount of the former decreases with decreasing CoO. With increasing Fe₂O₃ content, the color of the crystals seen in specimens etched with HNO₃ changes from dark yellow in the equimolecular composition to yellow for 2 CoO + 5 Fe₂O₃. With further increasing excess of Fe₂O₃, a new, light phase appears

along with the yellow crystals, attaining 45-50% in CoO + 6Fe₂O₃. By X-ray examination, free Fe₂O₃ is present in samples of the composition CoO + 3Fe₂O₃, and with higher Fe₂O₃ contents. The pure spinel structure of CoO + Fe₂O₃ persists up to Fe₂O₃ contents corresponding to 2 CoO + 5 Fe₂O₃. With excess CoO, from 3 CoO + 2 Fe₂O₃ upward, CoO lines appear along with those of the spinel CoO-Fe₂O₃. The latter is, consequently, the only compound occurring in this system. Fe₂O₃ is soluble in this ferrite to the extent of 1.5 mol. per mol. ferrite at 1,100°. CoO is not soluble in the ferrite.

3415. TORREY, P. D. Possibilities for Production of Liquid Fuels From Shale, Natural Gas, and Coal. I. *Petrol. Eng., Refining and Gas Processing Sec.*, vol. 22, No. 3, 1950, pp. A39-A44.

General review of present and future developments in the building of a synthetic liquid fuels industry. The long-range objective is considered, rather than immediate prospects.

3416. ———. Possibilities for Production of Liquid Fuels From Shale, Natural Gas, and Coal. II. *Petrol. Eng., Refining and Gas Processing Sec.*, vol. 22, No. 4, 1950, pp. A45-A48.

Discussion of coal reserves and the costs and possible production of liquid fuels from coal in the United States.

TORREY, R. M. See abs. 3227.

TOSHIMA, S. See abs. 1910.

3417. TOTZEK, F. Communication to the Power Commission, June 12, 1942. *TOM Reel 238*; Bureau of Mines transl. T-489, 1950, 20 pp.

Report on the complete gasification of powdered coal by the Koppers-Totzek process operating under fluidized conditions with the help of O₂ and steam. Experiments are described using both powdered lignite and bituminous coal for the production of synthesis gas. The results were particularly favorable. Using lignite, a gas of the following composition was obtained: CO, 14; CO₂, 35; H₂, 50; N₂, 1%; C + H₂ concentration 55%. Gas yield was 1.9 m³ per kg. of raw coal corresponding to an ideal gas yield of 1.62 N m³. O₂ consumption per kg. of coal was 1.304 N m³ corresponding to 0.16 N m³ per N m³ synthesis gas or 0.188 N m³ per N m³ ideal gas. The computed production cost of the synthesis gas was 1.32 pf. per N m³. With bituminous coal, the gas had the composition: CO, 11; CO₂, 54; H₂, 34; N₂, 1%; CO + H₂ concentration 88%. Gas yield was 2.1 N m³ per kg. coal, corresponding to an ideal gas yield of 1.55 N m³. O₂ consumption amounted to 0.525 N m³, corresponding to 0.25 N m³ per N m³ of synthesis gas or 0.284 N m³ per N m³ ideal gas. The cost was 1.72 pf. per N m³ synthesis gas. Similar calculations are made for the production of fuel gas from lignite, coal, lignite, and bituminous coal but without the use of O₂.

3418. TOWNEND, D. T. A. Gasification of Coal. *Gas World*, vol. 127, 1947, pp. 79, 406-418; *Chem. Age*, vol. 57, 1947, pp. 357-360, 399-400.

Paper presented at the St. Andrews symposium. An account is given of modern coal gasification developments with special attention to the Lurgi process as being typical of a pressure-operated process. Gasification uses internal heat normally by burning part of the charge with air or O₂. In the production of water gas, it is possible to combine the flow and make runs by using steam mixed with O₂ instead of air. Two main reactions may occur according to the temperature:

- (a) C + H₂O = CO + H₂ - 29 cal.
(b) C + 2 H₂O = CO₂ + 2 H₂ - 19 cal.

Reaction (a) occurs at 1,100° and (b) at 600°-700°. The temperature may be regulated by the rate of steam

flow. Working at a pressure of 20 atm. increases the amount of CH_4 , which is formed by a direct hydrogenation of the coal and not by synthesis, and this gives a higher calorific value to the gas; it also enables any CO_2 to be removed by scrubbing with H_2O . Such treatment gives a uniform gas independent of the type of coal used. The Lurgi process goes best with lignitic coal. The Lurgi process may be operated to produce synthesis gas for use in the Fischer-Tropsch reaction.

3419. ———. Recent Developments in Gasification. *Gas Times*, vol. 52, 1947, pp. 416-418; vol. 53, 1947, pp. 33-34, 37, 38.

William Young Memorial Lecture discusses the 2 main methods of producing gaseous fuels—carbonization and gasification. In the latter connection the discussion is confined mainly to the use of O_2 -steam blasts, the typical processes being the Lurgi pressure process, the Winkler boiling bed at atmospheric pressure, and the Leuna-type and Thyssen-Galocoy slagging producers operating at high temperatures with removal of the ash as slag. Some reference also is made to the Pintsch-Hillebrand and the Bubing-Didier processes, the Imperial Chemical Industries fluidized gas generator, and the Koppers powdered-fuel gasification process.

TRAEGER, B. See abs. 2693.

3420. TRAECKNER, K. [Gas Sources for the Present and Future Supply of Germany.] *Gas- u. Wasserfach*, vol. 82, 1939, pp. 590-595; *Chem. Abs.*, vol. 33, 1939, p. 9592.

Various suggestions as to methods of gas manufacture are reviewed after giving data as to present supply sources. The % of gas from brown coal has increased very little in the last 10 yr. in spite of much experimental work; the most successful plant is that at Kassel. Disadvantages of brown-coal carbonization processes are briefly reviewed, as well as the important features of a number of gasification processes. One of the more promising of these processes is that of gasification with O_2 under pressure. Results are given for 3 brown coals, showing gas and byproduct yields and net costs. This process also can use bituminous coals, which are noncaking when heated under pressure. The flexibility of this process is stressed, as well as the possibility of combining gas manufacture and hydrogenation or synthesis. In such cases, the rich residual gases can be used as an enriching medium for the manufactured gas.

3421. TRAMBOWZE, Y. [Chemical Changes in Fischer Catalysts During Their Preparation.] *Compt. rend.*, vol. 227, 1948, pp. 971-972; *Chem. Abs.*, vol. 43, 1949, p. 2853.

Catalysts were prepared by several methods, and the chemical nature of the Ni was determined by extraction with NH_4OH , with HNO_3 , and by fusion. Before reduction, Ni generally is found in 3 forms: The free oxide or combined with the CO ion, hydroaluminate, and hydrosilicate of Ni.

3422. ———. [Study of Fischer Catalysts by X-ray Diffraction.] *Compt. rend.*, vol. 228, 1949, pp. 1432-1433; *Chem. Abs.*, vol. 32, 1949, p. 7313.

Further study has been made of the Fischer Ni catalyst in an attempt to confirm the presence of both a hydroaluminate and a hydrosilicate of Ni. It is confirmed that the former coexists with the hydrosilicate at 450° .

3423. ———. [Chemical Changes in Fischer Catalysts During Their Preparation.] *Jour. chim. phys.*, vol. 47, 1950, pp. 258-261; *Chem. Abs.*, vol. 44, 1950, p. 7638.

Ni, Al, Mn, kieselguhr catalysts were prepared by the following methods, and the % of the Ni removed by ammoniacal treatment, extraction with HNO_3 , and with HCl , respectively, are: Precipitation at low tem-

perature, 100, —, —; boiling of the precipitate, 37, —; desorption under vacuum at 150° to constant weight, 63, 37, —; heating for 2 hr. at 220° in N_2 , 59, 13, 28; heating at 320° to constant weight in N_2 , 18, 46, 36; heating at 450° to constant weight in N_2 , 16, 40, 44; heating for 48 hr. at 220° in N_2 , 33, 59, 8; heating at 450° after the preceding treatment, 20, 59, 5, 20. An X-ray diffraction study of these catalysts is summarized.

3424. ———. [Relation of the Chemical Composition and Structure of Fischer Catalysts to Their Synthesis Activity.] Thesis, Univ. Lyon, France, 1950, 87 pp.

Previous discussions on the origin, structure, and reaction mechanism of the Fischer synthesis catalysts are reviewed. The paper consists of 2 parts. The 1st discusses the chemical changes that occur in the development of Ni base catalysts. The presence of the oxide and hydroxide of Ni, basic carbonates and hydroaluminate and -silicate of Ni was detected. These were measured by a polarographic method. The relative proportions of these various types of compounds can be changed markedly by changing the conditions of the thermal treatment preceding the reduction. For example, reheating for 48 hr. at 220° in a stream of N_2 strongly diminishes the content of silicate and may even prevent its formation totally. The 2d part discusses the effect of various chemical compositions on the catalytic activity of Fischer-Tropsch catalysts. The specific role of each individual compound mentioned above, and particularly those of Ni hydro-silicate and Ni hydroaluminate, are discussed, the latter being found particularly important.

3425. ———. [Study of Fischer Nickel Catalysts by Differential Thermal Analysis.] *Compt. rend.*, vol. 230, 1950, pp. 1169-1171; *Chem. Abs.*, vol. 44, 1950, p. 7132.

Ni hydroxide and the gel formed by precipitating Ni with K_2CO_3 are heated to 500° for 1.5 hr. Both show the dehydration of the hydroxide at 360° - 380° by a strong endothermic reaction; the second also shows the loss of adsorbed H_2O at 100° and the decomposition of the basic carbonates into CO_2 , H_2O , and NiO at 220° - 240° . Four other studies, one with a 1:1 mixture of kieselguhr and Ni hydroxide heated slowly, the other with catalysts heated variously to produce a silicate content of 15%, 8% and 0%, do not show the dehydration curve but do show the carbonate decomposition and, in the pertinent cases, another reaction at 400° , presumably hydrosilicate formation. When the contact mass is heated for a long time at 220° , the total decomposition of the basic carbonates and complete dehydration of the hydroxide make further combination impossible. A close relation between the precipitation conditions and the activity of a Fischer catalyst can now be established.

3426. TRAMBOWZE, Y., AND PERRIN, M. [The Effect of Preheating During the Course of Thermal Reduction of Nickel Catalysts on the Yield in the Fischer Synthesis.] *Compt. rend.*, vol. 228, 1949, pp. 837-839; *Chem. Abs.*, vol. 32, 1949, p. 8831.

It is clear that preheating clearly improved the activity of the 2 catalysts studied, the yield of hydrocarbons being tripled in the 1st case and doubled in the 2d. The % of reagents consumed is likewise maintained at a higher rate for a longer period. Furthermore, the active life of the catalyst is prolonged before poisoning takes place. It is established also that preheating not only raises the activity of the catalyst, which ordinarily is only medium, but also makes it superior to that of all catalysts not preheated. All these advantages result evidently from modifications occurring during the preheating. This is being investigated.

3427. ———. [Influence of the State of Combination of the Constituents of Nickel Catalysts on Their Activity in the Fischer Synthesis.] *Compt. rend.*, vol. 228, 1949, pp. 1015-1017.

Ratio of uncombined Ni to that present as the hydroaluminate is a determining factor in the activity of the Fischer synthesis, whereas the presence of the hydrosilicate is unfavorable to this activity. On the other hand, the more Ni there is combined in forms susceptible of easy reduction at 450° , oxides, carbonates, aluminate, the less is the hydrogenating activity. It is logical to admit that each compound of Ni put to use exerts its catalytic activity in a given direction, since it possesses a crystalline structure favorable to such a reactive process at the interface.

3428. ———. Effect of the Chemical Composition of Fischer Catalysts and Their Constituents on the Synthesis Activity. *Jour. Chem. Phys.*, vol. 47, 1950, pp. 474-482; *Chem. Abs.*, vol. 44, 1950, p. 9783.

Ni- Al_2O_3 -kieselguhr catalyst was shown to contain Ni aluminate and Ni silicate after being heat-treated to 450° . The aluminate is active in synthesizing higher hydrocarbons; the silicate forms CH_4 primarily. The distance between the Ni atoms in these 2 compounds is believed to be the factor responsible for the specificity of their catalytic properties.

3429. TRAMM, —. [Manufacture of Ethyl Benzene.] *FIAT Reel K24*, frames 3,127-3,130, Oct. 23, 1935; *PB* 70,215. *TOM Reel* 201.

Residue gas of the Fischer synthesis, the refuse gases of the gas-oil compression and the gases obtained in the cracking of gasolines are named as sources of ethane for manufacturing ethyl benzene. The % of ethane obtained and the cost for 1 ton of ethyl benzene are calculated.

3430. ———. [Plan of Pressure-Water Gas-Circulating Synthesis and the Low-Pressure Synthesis.] *FIAT Reel K24*, frames 3,069-3,076, Nov. 11, 1940.

Explains the scheme of the 2 types of synthesis in detail. The output of the obtained products is calculated. Two flowsheets.

3431. TRAMM, —, AND CLAR, —. [Preparation of Oils From Primary Products of the Gasoline Pressure Synthesis.] *FIAT Reel K29*, frames 6,634-6,701, 1940-1941; *PB* 70,218; *TOM Reel* 296.

Preparation of lubricating oils from gasolines of the pressure synthesis is described extensively. Primary materials are gasolines, which have been prepared partly by Co and partly by Fe catalysts. In any case, a preliminary treatment of the gasolines is necessary. The best way is to conduct the gasoline vapor through hot concentrated phosphoric acid with following neutralization. 26 tables, 3 graphs.

3432. TRAMM, H. [Gas Reactions in the Heavy-Chemical Industry.] *Rundschau deut. Tech.*, vol. 18, No. 23, 1938, p. 3; *Chem. Abs.*, vol. 32, 1938, p. 6509.

Reviews modern methods for the synthesis of technical products with the help of catalytic gas reactions, using especially H_2 , CO , N_2 , O_2 , C_2H_4 , C_2H_6 , C_2H_2 , and C_2H_4 . Illustrations.

3432a. ———. [Development of the Fischer-Tropsch Synthesis in Germany.] *Chem.-Ing.-Tech.*, vol. 24, 1952, pp. 181-182; *Chem. Abs.*, vol. 46, 1952, p. 6,361.

Bibliographical treatise in memory of F. Martin.

3432b. ———. [Industrial and Economic Possibilities of Carbon Monoxide Hydrogenation.] *Chem.-Ing.-Tech.*, vol. 24, 1952, pp. 237-247; *Bureau of Mines Transl. K-34*, 1952.

Recent developments of the Fischer-Tropsch process with fixed bed catalysts are presented. The report is limited to the work done by the Ruhrchemie-Lurgi

partnership. Great improvements in yield and quality of products and in gas-synthesis plant design have resulted from the development of high-activity catalysts and from the solution of important problems in reaction kinetics and heat transfer inside the reactors. As a result, the economic prospects of the process appear favorable for operation under German conditions. American prospects are discussed. The production of synthetic lubricants from the synthesis products is discussed in detail.

3432c. ———. [Technique of Carbon Monoxide Hydrogenation.] *Brennstoff-Chem.*, vol. 33, 1952, pp. 21-30; *Erdöl u. Kohle*, vol. 5, 1952, pp. 10-17; *Chem. Abs.*, vol. 46, 1952, p. 3,781.

Various types of converters used for hydrocarbon synthesis are illustrated and described. A graphic comparison shows the great improvement due to the modern high-capacity Fe catalyst as compared with the older Co catalyst. A graphic comparison of the total cost of gas manufacture by the blue-gas process with and without O_2 and with the producer-gas process, indicates that the water gas without the use of O_2 is the cheapest. For maximum gas utilization (96-97% conversion with low CH_4 formation) multiple-step conversion is required. Physicochemical investigations show that the gas for synthesis purposes should have a low CO_2 and H_2O content, but that N_2 is not as objectionable. CO_2 is chemisorbed on the catalyst but N_2 is only physically absorbed and is readily replaced. The undesirable effect of H_2O and CO_2 is shown graphically. A wide variety of products can be made by this process, ranging from gasoline to heavy wax, and including alcohols and their derivatives, solvents, and wetting agents. This wide range of products makes the process economically attractive in many countries.

See abs. 2591.

TRAPNELL, B. M. W. See abs. 2820.

3433. TRAUTZ, M., AND BADSTÜBER, W. [Vapor Pressure and Heat of Vaporization of Iron Pentacarbonyl.] *Ztschr. Elektrochem.*, vol. 35, 1929, pp. 799-802; *Chem. Abs.*, vol. 24, 1930, p. 3690.

Vapor pressure of $\text{Fe}(\text{CO})_5$ was measured 47.56° - 104.26° , by means of the apparatus of Trautz, Baisch, and Dechend. Calculations of the heat of vaporization, by the Clausius-Clapeyron equation, showed that it gradually decreased from 9.65 kcal. at 23.78° to 8.79 kcal. at 98.98° . From the pressures at 0° and 104.2° , a value of 9.38 kcal. is obtained—a value much higher than that of Dewar and Jones (*Proc. Roy. Soc.*, vol. 76, A, 1905, pp. 553-577). The lower values corresponding with the higher temperatures are attributed to the presence of $\text{Fe}_2(\text{CO})_9$, dissolved in $\text{Fe}(\text{CO})_5$, reducing its vapor pressure and raising its boiling point.

3434. TRAVERS, A. [Liquid-Fuel Problem and Proposed Solutions.] *Chim. et ind.*, vol. 13, 1925, pp. 373-382, 722-730; *Chem. Abs.*, vol. 19, 1925, p. 2398.

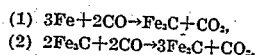
Discussion of the nature and distribution of petroleum, the processes of production of motor spirits from heavy oils or coal, cracking, berginization, synthesis from gaseous C compounds, and the situation in France.

3435. ———. [Methods of Increasing the Yield of Gasoline From Crude Petroleum. Substitute for Gasoline.] *Rev. ind. minerale*, vol. 15, No. 353, 1935, pp. 403-428; *Glückauf*, vol. 71, 1935, pp. 1277-1280; *Chem. Abs.*, vol. 29, 1935, p. 8304.

Nature of detrimental secondary reactions in the synthesis of MeOH from CO and H_2 is discussed together with the requirements of various catalysts. The energy consumption is about 1.8 kw.-hr. per kg. of pure MeOH . Theoretically, it is possible to form synthetic hydrocarbons representing 75-80% of the calorific value of water gas.

3436. TRAVERS, A., AND DIEBOLD, R. [Composition of Pure Cementite by Acids.] *Compt. rend.*, vol. 205, 1937, pp. 916-918; *Chem. Abs.*, vol. 32, 1938, p. 895. Large proportion, sometimes 78%, of C from cementite is liberated in the free state, while of the hydrocarbons evolved, paraffins (C_nH_{2n}) form only 3-4%, the rest being olefins (C_nH_{2n-2}) form only 3-4%, it is suggested, therefore, that cementite is (Fe₃C), with *n* not less than 3, and that the linkage: C:C is present, and that the H replacing the Fe on solution does not produce more than a small amount of saturated hydrocarbons on account of the absence of any catalyst. This view is shown to be consonant with several reactions and to explain the impossibility of determining (Fe₃C), by selective solution of Fe. The C separated is remarkably absorbent.
3437. ———. [Isolation of Pure Cementite by Acid Attack of Ferrous Materials and Some of Its Physical Properties.] *Compt. rend.*, vol. 205, 1937, pp. 797-799; *Chem. Abs.*, vol. 32, 1938, p. 895. Pure cementite, Fe₃C, was isolated from a white cast Fe (C, 3.4%; Si, 0.3; Mn, trace) by anodic attack in an acid medium or by simple acid (AcOH) attack (abs. 89) and separated from C by treatment with C₂H₄ (d. 1.47), washing with EtOH and Et₂O and drying in N₂. Thus obtained, it forms fine grains, greasy to the touch, Curie point 210°. The electrolytic potential relative to the calomel electrode (saturated KCl) is -0.820 for pH 2.3, -0.500 for pH 7.3. The potential of the couple Fe₃C-Fe is 0.230 at 48° in a neutral medium, but increases if the pH increases beyond 7.5.
3438. TREIBSTOFFWERK, RHEINPREUSSEN. [Sulfur in Synthesis Gas—Routine Analysis.] *MIS VII*, 67 g, 7003033, 1042, 310 pp; PB 17122. Manuscript data of the analyses made on gas at this synthetic oil plant in Germany is given. The analyses show S content before and after scrubbing and before entrance into the contact chamber.
- TREMEARNE, T. H. See abs. 150.
3439. TRILLAT, J. J., AND OKETANI, S. [Electron-Diffraction Study of the Cementation of Iron. I. Action of Pure Carbon Monoxide.] *Compt. rend.*, vol. 230, 1950, pp. 2,203-2,205; *Chem. Abs.*, vol. 44, 1950, p. 10,631. Extremely thin polycrystalline films were prepared by vaporizing from pure Fe or mild steel onto the surface of freshly cleaved rock salt; the salt was then dissolved in H₂O and the metallic film collected on a Ni grill. This was submitted to cementation in the presence of pure CO and then examined by electron diffraction. After cementation at 540°, orthorhombic crystals of cementite are present. Below 500° none is formed. At 540° if the preparations are not exposed constantly to fresh CO, decomposition takes place forming Fe₃O₄. As the temperature is raised, graphite is deposited on the surface, and above 820° the diagrams of Fe and Fe₃C are masked.
3440. ———. [Electron-Diffraction Study of the Cementation of Iron. II. Action of CO+H₂ Mixtures.] *Compt. rend.*, vol. 232, 1951, pp. 1116-1118. Supplementary studies to those performed with pure CO (see abs. 2719) and at slightly raised temperatures of 350°-400° have shown under the experimental conditions that only cementite Fe₃C and oxide Fe₃O₄ are formed. In the presence, however, of a mixture of equal parts CO+H₂ different results are noted. At 350° and for the duration of the reaction (1-2 hr.), the presence is indicated of α-Fe, a little cementite Fe₃C, and a compound characterized by a diagram different from that of cementite and sometimes appearing in the pure state. Detailed examination identifies it as the percarbide Fe₅C or Hägg carbide. At 400°, after

a 1-hr. treatment by CO+H₂, only cementite Fe₃C and α-Fe appear. The percarbide may however be seen if the reaction is prolonged to 2-3 hr. Above 400° only cementite exists. The results thus seem to indicate that the percarbide ceases to be stable above 400° while the cementite exists up to at least 600°. In the stable regions of percarbide, the following reactions probably occur:



The formation of percarbide follows that of cementite, which contains less C; up to 400° reaction (2) may occur but not above. The presence of H₂ accelerates the speed of the reaction considerably. Further studies will be made of the action of CO+H₂ at temperatures below 350° and above 600°.

3440a. ———. [Electron-Diffraction Study of Cementation of Iron by Carbon Monoxide.] *Métaux et corrosion*, vol. 25, 1950, pp. 263-264; *Chem. Abs.*, vol. 45, 1951, p. 9440.

One hour cementation in CO atmosphere at 540° forms the orthorhombic Fe₃C; however, at temperatures <500° no Fe₃C was observed. During cementation in CO or in air there is a spontaneous oxidation of Fe forming Fe₃O₄ film perpendicular to the prepared surface. During cementation at higher temperatures graphite is deposited on the prepared surface. Above 820° there is no evidence of either Fe₃C or Fe which without doubt are masked by the graphite. Samples previously oxidized in air and then carburized at 540° give the same results but the cementite grain size is greater.

TROELTSCH, J. See abs. 1677.

3441. TROESCH, A. [Inhibition by Carbon and Hydrogen of the Adsorptive Activity of Methane by Fischer Nickel Catalysts.] *Compt. rend.*, vol. 228, 1949, pp. 1013-1015; *Chem. Abs.*, vol. 43, 1949, p. 6064.

Previous work on the adsorption of CH₄ on Ni catalysts is reviewed, and new experiments are analyzed. The adsorption of CH₄ upon the Fischer Ni catalyst is inhibited both by C, the fixation of which by the catalyst diminishes the active surface without modifying the speed of adsorption, and by H₂, the presence of which in the adsorbent reduces simultaneously the active surface and the speed of adsorption.

3442. ———. [Kinetic Laws of Adsorption of Methane by Fischer Catalysts Containing Nickel.] *Compt. rend.*, vol. 228, 1949, pp. 1126-1128; *Chem. Abs.*, vol. 43, 1949, p. 6064.

Previously published results (abs. 3441) were analyzed kinetically. The heat of adsorption of CH₄ on a Fischer catalyst approximated 17 kcal. per mol.

3443. ———. [Application of the Kinetic Laws of Adsorption and Desorption to the Study of Catalysts.] *Jour. chim. phys.*, vol. 47, 1950, pp. 148-156; *Chem. Abs.*, vol. 44, 1950, p. 8754.

Measurements of the rate of desorption of H₂ indicate 3 types of active centers for which energies of activation of desorption are 9, 12, and 16.8 kcal., respectively. The action of adsorbed H₂ and C on the kinetics of CH₄ adsorption on Ni as published previously (abs. 3441 and 3442) is discussed.

3444. ———. [Dissociation of Methane in Presence of a Nickel Catalyst.] *Jour. chim. phys.*, vol. 47, 1950, pp. 274-285; *Chem. Abs.*, vol. 44, 1950, p. 7637.

Studies made in the absence and presence of a Ni catalyst indicate that no reaction took place between CH₄ and Ni at 112°-237°. No intermediate carbide is necessary to explain the decomposition. The evidence suggests that Ni carbide is not responsible for the efficacy of Fischer-Tropsch catalysts.

3445. ———. [Kinetic Equations for Adsorption and Desorption.] *Jour. chim. phys.*, vol. 47, 1950, pp. 145-147; *Chem. Abs.*, vol. 44, 1950, p. 8104.

Adsorption of CH₄ on a Ni-Al-Mn-kieselguhr catalyst (abs. 2608) obeys a simple Langmuir rate equation in which desorption is neglected and the rate of adsorption is proportional to the fraction of the surface not covered by adsorbate. The rate of adsorption of H₂ does not follow such an equation but indicates that the surface is heterogeneous. Desorption of CH₄ from the Ni surface at 170° and a constant pressure of 10⁻⁴ mm. cannot be measured because the evolved gas is all H₂. The rate of H₂ desorption does not follow the simple Langmuir equation and again indicates surface heterogeneity.

TROITSKAYA, F. B. See abs. 3764, 3766.

3446. TROPSCH, H. [Synthesis and Decomposition of Formates.] *Ann. chim. phys.*, vol. 15, No. 9, 1921, pp. 42-60.

Investigation of CaO as a catalyst for reactions in water gas mixtures was extended, and a study was made of the synthesis and decomposition of formates. As regards the mechanism of CH₄ synthesis, it is assumed that at temperatures below the decomposition of CaCO₃ (900°) water gas reacts with CaO to give calcium formate. CaO+2 CO+H₂O=Ca(CHO)₂. The formate in the presence of an excess of lime then reacts to give CH₄ and CaCO₃. 2 Ca(CHO)₂+CaO=3 CaCO₃+CH₄.

3447. ———. [Decomposition of Synthol at Atmospheric Pressure.] *Gas. Abhandl. Kenntnis Kohle*, vol. 7, 1925, pp. 49-50; *Chem. Abs.*, vol. 21, 1927, p. 1698.

Synthol, 5.8 gm., on heating to 400°-480° at atmospheric pressure yielded 3.9 gm. C, 0.3 gm. CO₂, 0.7 gm. CO, 0.5 gm. H₂, 0.2 gm. CH₄, and 0.1 gm. hydrocarbons, these products being different from those obtained by heating it under pressure in autoclaves (abs. 1014).

3448. ———. [Higher Boiling Constituents of Synthol.] *Gas. Abhandl. Kenntnis Kohle*, vol. 7, 1925, pp. 75-77; *Chem. Abs.*, vol. 21, 1927, p. 2779.

Higher-boiling constituents of Synthol contain small quantities of viscous oils, which can be acetylated and, therefore, contain hydroxyl groups. The least volatile constituents are solid and asphaltic. Traces of a solid, paraffinic substance are obtained also.

3449. ———. [Equilibrium Conditions in the Formation of Hydrocarbons and Alcohols From Water Gas.] *Brennstoff-Chem.*, vol. 8, 1927, p. 376; *Gas. Abhandl. Kenntnis Kohle*, vol. 8, 1929, pp. 336-337; *Chem. Abs.*, vol. 22, 1928, p. 3976.

Smith states (abs. 3206) that equilibrium calculations show that, as the temperature is increased, formation of higher rather than lower hydrocarbons is favored, whereas experimental work of Tropsch shows that high temperatures favor formation of CH₄. Smith also finds that increased pressure favors production of higher paraffins. This agrees with experimental results of Tropsch, except that oxygenated compounds are formed at temperatures high enough to drive from the catalyst the higher hydrocarbons, which have been formed.

3450. ———. [Equilibrium Conditions for Formation of Hydrocarbons and Alcohols From Water Gas.] *Brennstoff-Chem.*, vol. 9, 1928, p. 250; *Chem. Abs.*, vol. 22, 1928, p. 4773.

Comment on abs. 3208.

3451. ———. [Manufacture of Butyl Alcohol, Acetone, and Methanol From Corn.] *Brennstoff-Chem.*, vol. 9, 1928, pp. 1-2; *Chem. Abs.*, vol. 22, 1928, p. 2635.

Description of the Commercial Solvents Co. process at Peoria, Ill. The mixture of 60% CO₂ and 40% H₂ liberated during fermentation is washed with water under pressure to bring the proportion to 25% and 75%, respectively, and is then compressed to 300 atm., and passed over a catalyst comprising 97.75% Zn or Mg oxide with 3.25% Fe₂O₃. From the mixture of 68% MeOH and 32% H₂O, pure MeOH is obtained by rectification. Thirteen tons of MeOH are produced per day.

3452. ———. [Conversion of Coal Into Oils.] *Gas. Abhandl. Kenntnis Kohle*, vol. 8, 1929, pp. 348-353; *Chem. Zentralb.*, 1929, II, p. 3266; *Chem. Abs.*, vol. 24, 1930, p. 5461.

Survey of the known methods of producing liquid fuels from mineral coals either directly or indirectly by primary gasification.

3453. ———. [Problems in Fuel Chemistry.] *Gas. Abhandl. Kenntnis Kohle*, vol. 8, 1929, pp. 393-406.

Review of the methods of producing liquid fuels.

3454. ———. [Composition of the Products Obtained in the Synthesis of Petroleum.] *Gas. Abhandl. Kenntnis Kohle*, vol. 9, 1930, pp. 561-570; *Chem. Abs.*, vol. 25, 1931, p. 3806.

Benzene fraction, boiling at 60°-135°, of the synthetic petroleum obtained by the catalytic reduction of CO at ordinary pressures has been examined (abs. 1021).

After fractionating at every 10°, the specific gravity, *n*, and *I* value of each fraction were determined. The olefins were determined by separation as the double compound with Hg acetate, being subsequently regenerated by dilute HCl. The benzene was found to consist almost entirely of a mixture of paraffins, *n*-pentane to *n*-nonane, also *iso*-nonane, with the corresponding olefins, the latter predominating, especially in the lower-boiling fractions. It was quite stable to air and light for at least 2 yr.

3455. ———. [Synthesis of Organic Compounds From Gases Obtainable From Coal.] *Entstehung, Veredlung und Verwertung der Kohle*, Berlin, Bornträger, 1930, 359 pp., chap. V.

See abs. 1013, 1014, 1015, 1016, 1017, 1018, 1019, 1020, 1021, 1022, 1023, 1024, 1025, 1026, 1043, 1044, 1045, 1046, 1047.

3456. TROPSCH, H., AND DITTRICH, E. [Analysis of Gaseous Hydrocarbons, Particularly Olefins.] *Brennstoff-Chem.*, vol. 6, 1925, pp. 169-177; *Gas. Abhandl. Kenntnis Kohle*, vol. 8, 1929, pp. 285-304; *Chem. Abs.*, vol. 19, 1925, p. 2703.

Fractional condensation at liquid-air temperatures was applied in the analysis of complex mixtures of paraffins and olefins. Gases other than hydrocarbons are first determined (CO₂ by absorption in KOH, O₂ with alkaline pyrogallol, CO with ammoniacal CuCl₂ and H₂ by selective combustion over CuO heated to 240°, at which temperature it is shown the higher hydrocarbons are not affected) and the residual hydrocarbons are then condensed by liquid air in an apparatus built by Ströhlein Co. Düsseldorf. Condensation and fractionation are carried out in 4 U-tubes cooled to suitable temperatures by liquid air and also by Al blocks cooled by this medium. The fractionation is carried out under high vacuum maintained by a Töppler pump. A Gaebe pump is used also to circulate gases. The fractions obtained are: B (CH₄), C₁ (ethane, propane, ethylene, and propylene), C₂ (propane, butane, propylene, and butylene), D (olefins and paraffins of higher molecular weight). From the individual fractions, ethylene homologs are absorbed by 87% H₂SO₄ and ethylene itself is absorbed by a mixture of solutions *a* and *b* in proportions 0.25:1.875, *a* being 87% H₂SO₄ saturated with NiSO₄ and *b* being 87% H₂SO₄ containing 0.6%

- Ag₂SO₄. The amount of C corresponding to each vol. absorbed is determined by oxidation of the acid solution with excess KIO₄ and back titration of the excess with Na₂S₂O₄. Paraffin hydrocarbons are determined by combustion in small quartz tubes containing heated CuO. Boiling curves of the hydrocarbons are given with numerous tables of analytical data for pure gases. Specimen analyses of (1) an oil gas, (2) a synthol gas, and (3) a gas from the Bergius hydrogenation process are given.
3457. TROPSCH, H., AND KASSLER, R. [Catalytic Properties of Rhenium.] Ber. deut. chem. Gesell., vol. 63 B, 1930, pp. 2149-2151; Chem. Abs., vol. 25, 1931, p. 22.
- Reduced Re and Re-Cu catalysts act as hydrogenating catalysts in the reactions CO-OH, and C₂H₄-C₂H₆. At 470°, Re carbide is formed by passing CO over a Re-Cu catalyst.
3458. TROPSCH, H., AND KOCH, H. [Synthetic Benzene From Water Gas.] Brennstoff-Chem., vol. 10, 1929, pp. 337-346; Petroleum (London), vol. 26, 1930, pp. 157-158; Ges. Abhandl. Kenntnis Kohle, vol. 9, 1930, pp. 533-560; British Chem. Abs., 1929, B, p. 1003; Chem. Abs., vol. 24, 1930, p. 4919.
- Synthetic benzene obtained from water gas by catalytic reduction at atmospheric pressures was a mixture of 65% olefins, 0.1% benzene, 0.4-0.5% toluene and paraffins. The saturated and unsaturated constituents were separated, isolated, and identified in various fractions of the carefully fractionated benzene; a modified Eg acetate method was used whereby pure olefins were obtained from mixtures containing saturated hydrocarbons. The hydrocarbons thus obtained were pentane, hexane, heptane, octane, 3-methyloctane, nonane, 1-pentene, 2-pentene, 1-hexene, 2-hexene, 3,3-dimethyl-1-pentene, heptene, 2-octene, and nonene. A long-needed crystalline substance melting 106°, of unknown composition but possibly a γ-pyrone derivative, separated from the 100°-120° fractions of the benzene.
3459. TROPSCH, H., AND KRÖNIG, W. [Observations on the Action of Carbon Monoxide on Iron Oxide.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 46-48.
- It is concluded that the formation of synthol by way of the carbide from Fe and CO is not probable.
3460. TROPSCH, H., AND SCHELLENBERG, A. [Formation of Methane in the Water-Gas Process.] Brennstoff-Chem., vol. 3, 1922, pp. 33-37; Ges. Abhandl. Kenntnis Kohle, vol. 6, 1921, pp. 317-329; Chem. Abs., vol. 16, 1922, p. 2022.
- Vignon's experiments (abs. 3560, 3561, 3562, 3563), on the reduction of CO to CH₄ by means of H₂ in the presence of CaO and Fe, at 900°-1,000° have been repeated and only traces of CH₄ found. The presence of 25-30% CH₄ among the products of dry distillation of Ca(HCOO)₂ could likewise not be confirmed. Vignon apparently determined CH₄ by difference and did not allow for residual N₂ in the apparatus.
3461. ———. [Decomposition of Methanol by Iron, Tin, and Aluminum.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 13-14; Chem. Zentrbl., 1926, I, p. 3298; Chem. Abs., vol. 21, 1927, p. 3530.
- MeOH vapor was conducted over the metal heated and spread out with a combustion tube. At 520°, C was deposited on the Fe, decomposition of the MeOH to a gas containing 4-7% CO₂, 20-25% CO, 55-60% H₂, and 3-12% CH₄ occurring. The small quantity of condensate was neutral and contained HCHO. With tinned Fe, the decomposition of MeOH followed the same course but was only slight. With Al at 520°, the gas contained 5% CO, 23% CO₂, 60% H₂, and 4% CH₄, and, at 270°, it contained 2% CO₂, 5% CO, 52% H₂, and 30% CH₄. In a receiver cooled with liquid air, a reaction product containing Al, probably AlMe, condensed.
3462. TROPSCH, H., AND VON PHILIPPOVICH, A. [Comparative Experiments on the Decomposition of Carbon Monoxide by Contact Substances.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 44-45; Chem. Zentrbl., 1926, I, p. 3298; Chem. Abs., vol. 21, 1927, p. 3530.
- Purified and dried CO was conducted over contact substances at 400°. Its decomposition according to the reaction: 2CO → CO₂ + C, was measured by determining the CO. Ni was the most active catalyst, but this activity was almost completely destroyed by alloying the Ni with 50% Sn. Great differences were found among different types of Fe. With a CO current of 400 cc. per hr., the following % CO₂ were found in the issuing gas: with Ni, 36.4; Fe from Fe₂O₃, 10.4; ferr. reduct., 2.3; ZnO, 0.9; MnO, 0.8; Cr₂O₃, 0.6; NiSn, 0.3-0.6; Al₂O₃, 0.4; BaSO₄, 0.4; tinned Fe, 0.4; MgO, 0.2; Cu, 0.0.
3463. ———. [Condensation of Methanol in the Presence of Contact Substances.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 75-83; Chem. Abs., vol. 21, 1927, p. 2870.
- Catalysts examined were those used in the production of synthol, with a view to elucidate the mechanism of this reaction. In nearly all cases, a small quantity of an oil of terpenelike odor was obtained, and the possibility of the formation of higher boiling compounds was proved. With NaOMe, Me₂O was formed, and the reaction gas was composed almost exclusively of H₂. In all other cases, considerable quantities of CH₄ were produced. With an alkaline Fe catalyst, a considerable amount of oily products was obtained, proving the production of oils directly from MeOH to be possible.
3464. TROPSCH, H., SCHELLENBERG, A., AND VON PHILIPPOVICH, A. [Reduction of Carbon Monoxide.] Ges. Abhandl. Kenntnis Kohle, vol. 7, 1925, pp. 63-67; Chem. Abs., vol. 21, 1927, p. 2550.
- Formation of CH₄ from a mixture of CO (1 vol.) and H₂ (3 vol.) in contact with Ni, which normally occurs quantitatively at 240°-250°, is greatly diminished by adding NH₃ to the gas mixture. Neither formaldehyde nor hexamethylenetetramine was formed, and the final mixture contained 13% CH₄, 15% CO, 64% H₂, and 8% Ni. With a Ni catalyst that had been treated with alkali, the same gas mixture yielded at 400° and atmospheric pressure, 53% CH₄ and 1.1% of unsaturated hydrocarbons, the only liquid reaction product being H₂O. The same reaction occurred with a Ni catalyst that had not been treated with alkali, except that no unsaturated hydrocarbons were formed. A mixture of equal volumes of CO and H₂ in contact with an alkaline Ni catalyst at 400°, deposited much C. With a feebly alkaline catalyst, the final gas contained 27% CO₂, 2% CO, 26% H₂, and 45% CH₄, while, with a more strongly alkaline catalyst, it contained 11% CO₂, 29% CO, 50% H₂, and 9% CH₄. With both alkaline and neutral catalysts, the CH₄ contained 1.5% of higher homologs, reckoned as ethane. A mixture of equal volumes of CO and H₂ in contact with neutral Ni at 400°, gave a final gas containing 10% CO₂, 42% H₂, and 48% CH₄, while with alkaline Ni it gave 7% CO₂, 70% H₂, and 23% CH₄. In no case could MeOH be detected.
3465. TRÜCKER, R. [Industrial Synthesis of Fat Acids.] Rev. sci., vol. 80, 1942, pp. 265-270; Chem. Zentrbl., 1943, II, p. 1511; Chem. Abs., vol. 38, 1944, p. 6273.
- Review of the development of processes, difficulties encountered, and means of overcoming them.
- TSILINSKAYA, T. F. See abs 703, 2887.
- TSUNEOKA, S. Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXI. Relations of the Gas Composition to the Working Temperature and to the Degree of Saturation of the Benzene, Respectively. See abs. 1857.

- Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXII. Usefulness of a New Alloy Catalyst. See abs. 1858.
- See abs. 1850, 1851, 1852, 1853, 1854, 1855, 1856, 1866, 1867, 1869, 1874, 1877, 1884, 1885, 1908.
3466. TSUNEOKA, S., AND FUNASAKA, W. Purification of the Gaseous Raw Material Used for Benzene Synthesis. I. Removal of Organic Sulfur Compounds at Low Temperature. Jour. Soc. Chem. Ind. (Japan), vol. 41, B, 1938, pp. 43-47; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 301-309 (in German); Chem. Abs., vol. 32, 1938, p. 3577.
- Researches were undertaken to find a satisfactory method of S removal, with known or new materials, from a gas to be used further for the synthesis of benzene, its S contents to be less than 0.2 gm. per 100 m³ city gas, with a total S content of 24.0 gm. S per 100 m³, of which 22.6 gm. S is organic, was freed of CO and H₂S and, as such, used over adsorbent materials, dry purificants, and H₂S extraction materials at room temperature. As adsorbent materials were used active C, SiO₂ gel, Japanese acid earths, and Adosol. Active C was found the most efficient but not active enough to produce a highly purified gas. As dry purificants, Fe₂O₃ on a pumice support and Luxmasse were used; as H₂S scrubbing materials, Thylox soluble and (C₂H₅)₂N, to which Fe₂O₃ was added, were used. 80% S removed was obtained with the dry purificants. Thylox failed to extract the organic S, while, with (C₂H₅)₂N, 67.7% S removal was obtained; it was further improved by addition of Fe₂O₃.
3467. ———. Purification of the Gaseous Raw Material Used for Benzene Synthesis. II. Removal of Organic Sulfur Compounds at High Temperature. Jour. Soc. Chem. Ind. (Japan), vol. 41, B, 1938 pp. 47-51; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 34, 1938, pp. 310-320 (in German); Chem. Abs., vol. 32, 1938, p. 3577.
- The same city gas was used for S removal at high temperature by passing the gas through heated pipes without and in the presence of catalysts. Fe, Cu, and V₂A steel pipes were used. At 500°, Fe pipe gave the best results but desulfuration is only 77%. Ag catalysts, 1% Ag by weight, CuO-CrO₂-Pb, Ni, Fe-Cu, Ag catalysts, 10% metal, and active C were used in an effort to eliminate the organic S by transforming it into H₂S, by contact. With CuO-CrO₂-Pb, Ni, Fe-Cu catalysts, 10% metal, at temperatures 450°, 350°, 300°, 330 cc. per hr. per cc. contact (Ges. Abhandl. Kenntnis Kohle, vol. 10, p. 313) in each case, the organic S content was reduced to less than 0.2 gm. per 100 m³ of gas. The amount of organic S changed into H₂S was very small, the major part of it being fixed on the catalyst. A preliminary extraction of H₂S from the gas is necessary, otherwise the amounts of total S, remaining in gas, are 0.66, 3.12, 0.82 gm. per 100 m³, respectively. With Fe₂O₃ on a pumice support, 30% Fe₂O₃, and Luxmasse, at 350° and 330 cc. per hr. per cc. contact, the organic S was completely removed from the gas. No preliminary extraction of H₂S is necessary, and the S is economically removed to less than 0.2 gm. S per 100 m³, organic S less than 0.07 gm. per 100 m³, total S less than 0.07 gm. per 100 m³, or 99.7% S removed. The Luxmasse used by the authors was a byproduct obtained in the manufacture of Al, red mud, often used in city gas plants for H₂S removal, which in muddy form contained 38.2% of H₂O. The material was dried for 12 hr. at 105° and then crushed to 3-5 mm. granules.
- TSUNEOKA, S., AND FUNASAKA, W. Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLII. Purification of the Gaseous Raw Material Used for Benzene Synthesis.
1. Removal of Organic Sulfur Compounds at Low Temperature. See abs. 1878.
- Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLIII. Purification of the Gaseous Raw Material Used for Benzene Synthesis. 2. Removal of Organic Sulfur Compounds at High Temperature. See abs. 1879.
- TSUNEOKA, S., AND KURODA, R. Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIV. Analytical Studies of Alloy Catalysts. See abs. 1870.
- Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXV. Microscopic Study of Alloy Catalysts. See abs. 1871.
- Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVII. Cobalt Alloy Catalysts. See abs. 1863.
- TSUNEOKA, S., AND MURATA, Y. Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIII. Extraction and Leaching Treatment of Alloy Catalysts. See abs. 1859.
- Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVI. Gas Contraction and Benzene Synthesis. See abs. 1862.
- Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXV. General Properties and Constituents of the Benzene Prepared With an Alloy Catalyst. See abs. 1861.
- Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIX. Influence of Bore and Length of the Reaction Tube. See abs. 1865.
- Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXIV. Influence of the Particle Size and the Hydrogen Treatment or Oxidation Conditions of the Alloy Catalysts. See abs. 1860.
- Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXVIII. Nickel-Alloy Catalysts. See abs. 1864.
- Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIX. Properties of a Precipitated Nickel-Cobalt Catalyst. See abs. 1875.
- Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XL. Proportions of Nickel and Cobalt, and the Influence of the Addition of Copper to the Precipitated Nickel-Cobalt Catalysts. See abs. 1876.
- Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXII. Studies on the Material of the Reaction Furnace. See abs. 1868.
- Synthesis of Benzene From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVI. Relation of the Activity of the Catalyst to the Synthesis Requirements at too High a Temperature. See abs. 1872.
- TSUNEOKA, S., AND NISHIO, A. Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVII. Volume Velocity of the Gas. See abs. 1873.
- Synthesis of Benzene From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVII. Composition of Starting Gases with New Iron Catalyst. See abs. 1883.
- TSUNEOKA, S., MURATA, Y., AND MAKINO, S. Synthesis of Benzene From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVI. Preparation of New Iron Catalysts and Their Superior Properties. See abs. 1882.

3468. TSUNEOKA, S., MURATA, Y., FUNASAKA, W., AND NISHIO, A. Fischer Process—Japan. Jour. Fuel Soc. Japan, vol. 18, 1939, p. 47.

Continuous investigations were carried out by the Imperial Fuel Research Institute on:

(1) Studies on gas space velocity. The yield of gasoline was maximum at a certain gas velocity, either when the amount of the catalyst and the length of the catalyst zone or the gas space velocity and the length of the catalyst zone were maintained constant. The content of unsaturated hydrocarbons in the synthesized gasoline increased with an increase of gas velocity.

(2) The relation between the degree of unsaturation of the synthesized gasoline and various conditions.

(3) Studies on Ni-Co catalysts prepared by the precipitation method. U_2O_5 and ThO_2 were found to be superior promoters both for Ni-Co (50:50) and Ni-Co-Mn (50:50:15) catalysts; the yield of gasoline was 160 cc. per m.³ with Ni-Co-Mn- U_2O_5 - ThO_2 -kieselguhr (50:50:15:5:3:125) and 179 cc. per m.³ with Ni-Co-Mn- U_2O_5 -kieselguhr (50:50:20:20:125) catalysts. The optimum ratio of Ni:Co was found to be 50:50. The reduction temperature of a Ni-Co-Mn- U_2O_5 - ThO_2 -kieselguhr (50:50:15:5:3:125) catalyst was lowered from 400° C. to 300° C. owing to the addition of 10% of Cu, notwithstanding that the activity was depressed greatly.

(4) Removal of organic S compounds from industrial gas. The content of organic S compounds in coal gas was reduced from 22.6 gm. S per 100 m.³ to 0.2 gm. S per 100 m.³ and less by the use of $CuO-PbCrO_4$, Ni, and Fe-Cu catalysts at temperatures of 450°, 350°, and 300° C. and the same space velocity of 330. The organic S compounds in coal were quantitatively fixed with Fe_2O_3 on pumice and Luxmasse at a temperature of 350° C. and a space velocity of 330, the content of S being reduced to 0.2 gm. S per 100 m.³ and less.

(5) Activation of a gasoline catalyst by slow oxidation with air. The activity of a Ni-Co-Mn- U_2O_5 - ThO_2 -kieselguhr (50:50:15:5:3:125) catalyst was increased by about 10% and 8%, respectively, when the catalyst, after reduction at 400° C. was oxidized slowly with air directly or after the replacement by H_2 with CO_2 .

(6) Studies on Fe catalysts prepared by the precipitation method. Fe-Cu catalysts, prepared by the precipitation method, were studied, and 94 cc. per m.³ ($CO:H_2=1$) of gasoline was obtained with a Fe-Cu-Mn- Al_2O_3 -kieselguhr- K_2CO_3 (100:25:2:3:125:2) catalyst.

3469. TSURUMI, S. Synthesis of Benzene From Carbon Monoxide and Hydrogen. Jour. Fuel Soc. Japan, vol. 12, 1933, pp. 1383-1390 (in English, pp. 137-138); Chem. Abs., vol. 28, 1934, p. 1515.

Previous work of Fischer and Tropsch and of Fujimura is reviewed and the author's own data presented. The highest yield attained by Fujimura was 145 cc. of liquid product per m.³ mischgas with 33 parts CO and 67 of H_2 . The catalyst consisted of Co:Cu:Th:U=S:1:0.2:0.1. The author obtained a yield of 155 cc. per m.³ of mischgas. Details of the work and the composition of the catalysts will be presented in a later paper.

3470. Synthetic Gasoline From Carbon Monoxide and Hydrogen. I. Rept. Imp. Fuel Research Inst. Japan, No. 31, 1935, 62 pp.; Jour. Fuel Soc. Japan, vol. 14, 1935, pp. 110-116 (in English); Brennstoff-Chem., vol. 17, 1936, p. 54; Chem. Abs., vol. 29, 1935, p. 7627; vol. 30, 1936, p. 845.

Gas mixture consisting of 1 part CO and 2 H_2 was used for the investigation. The effect of various factors on the course of the synthesis was investigated with a Co:Cu:U₂O₅:kieselguhr (1:0.1:0.12:1) catalyst. With this catalyst the highest yield, namely 97 gm. per m.³ mischgas, was obtained at 210°.

With rising temperature the formation of gaseous hydrocarbons decreased. The most favorable gas velocity was 3-6 l. per hr., using 3 gm. Co. A gas mixture of 1 CO and 2 H_2 gave the best yield per m.³ of synthesis gas. With a gas rich in H_2 the reaction temperature can be lowered; this reacts favorably on the life of the catalyst. A ratio of Co:kieselguhr=1:1 or 3:4 made the most active catalyst. Besides kieselguhr, alumina, pumice, and silica gel were used as carrier material; in no case was the activity equal to that with kieselguhr. The best raw material for the preparation of the catalyst was the nitrate. The catalyst prepared from the acetate was equal in activity, whereas that made from the sulfate was less active. When the chloride was used, the catalyst was virtually inactive. Further tests were performed with Ni:Mn catalysts. The best results here were obtained with a Ni catalyst to which 20% Mn, 8% U_2O_5 , and 4% ThO_2 were added. The maximum yield amounted to about 115 gm. of liquid product per m.³ of mischgas. With a mixed catalyst of Co:Ni:Cu the results were more unfavorable, the activity decreasing with increasing content of Ni and Cu. The reason for this behavior lies in the formation of mixed crystals between Ni and Cu. The mechanism of the reaction is discussed from the standpoint of carbide formation. Mention is made in this connection that with mixtures of CO_2 and H_2 higher hydrocarbons are not formed, only CH_4 . No carbide formation was observed.

3471. Promoting Action of a Catalyst Promoter and Carrier. I. Jour. Chem. Soc. Japan, vol. 57, 1936, pp. 685-691; Chem. Abs., vol. 30, 1936, p. 7436.

Synthesis of liquid hydrocarbons from CO and H_2 is studied. For catalysts that require no high temperature before reduction of CO with H_2 and cause reaction at approximately 200°, no accelerating action of the carrier is noticed, but it has a tendency to decrease the activity of the catalyst. For catalysts that require high temperature before the reaction, the presence of carrier gives much acceleration, increases the resistance to heat, and increases the activity of the catalyst. There is no fundamental difference between carrier and accelerator in increasing the resistance of the catalyst to heat. The temperature of reduction increases with an increase in amount of carrier and accelerator, and an increase in small amount of accelerator gives the result of using a large amount of carrier when it is estimated by an increase in the temperature of reduction.

3472. Studies of the Promoting Action of a Catalyst Promoter and Carrier. II. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 63-70; Chem. Abs., vol. 31, 1937, p. 2915.

Effect of the calcining temperature upon the gas-absorbing power of the mixtures $Co+Cu+U_2O_5$ in the range 200°-300°, and $Co+U_2O_5$, $Co+ThO_2$ in the range 250°-450° containing various amounts of diatomaceous earth was studied. The gas used was the mixture $CO+H_2$ in the ratio 1:2. The proper temperature to get the maximum absorbing power does not change much with the amount of the diatomaceous earth.

3473. Studies on the Promoting Action of a Catalyst Promoter and Carrier. III. Selection of the Catalyst for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 996-1001; Chem. Abs., vol. 32, 1938, p. 735.

It has been stated that, in the reaction between CO and H_2 , the active power of the catalyzer greatly depends on the mode of preparation.

3474. Studies on the Promoting Action of a Catalyst Promoter and Carrier. IV. Activity of the

Catalyst for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 1002-1006; Chem. Abs., vol. 32, 1938, p. 735.

3475. Promoting Action of Promoter and Carrier. V. Changes on the Catalyst Surface Caused by the Addition of Promoter and Carrier. Jour. Chem. Soc. Japan, vol. 59, 1938, pp. 893-898; Chem. Abs., vol. 32, 1938, p. 7322.

Most suitable % of Cr and of diatomaceous earth in the catalyst Ni-Cr-diatomaceous earth, for the synthesis of liquid hydrocarbons from CO and H_2 are 7.5% and 50%, respectively.

3476. Promoting Action of Promoters and Carriers. VI. Relation Between the Dispersity of Catalysts and the Catalytic Activity. Jour. Chem. Soc. Japan, vol. 59, 1938, pp. 1407-1411; Chem. Abs., vol. 33, 1939, p. 2200.

In the catalytic reduction of C_6H_6 , the catalyst prepared by the following method is most effective. To the solution of $Co(NO_3)_2$, a slight excess of K_2CO_3 is added. The precipitate is dried at 200°, mixed with kieselguhr and H_2O in a mortar, and dried at 100°. The ratio of Co to kieselguhr is 1:40. This method of preparation can be applied to the catalyst having the composition (4 Ni+Co)+7.5% Cr in the synthesis of liquid hydrocarbons from CO and H_2 .

3477. Preparation of Water Gas From Methane. Repts. Imperial Fuel Research Inst., Japan, No. 34, 1937, 50 pp.; Jour. Fuel Soc. Japan, vol. 17, 1938, pp. 24-28; British Chem. Abs., vol. 57, 1937, B, p. 751; Chem. Abs., vol. 32, 1938, p. 3125.

Experimental procedure and various factors, such as catalysts and temperature affecting the reactions, are given in detail with experimental data.

3478. Production of Carbon Monoxide and Hydrogen by Means of the Methane-Steam Reaction. I. Action of a Nickel Catalyst on the Water-Gas Reaction. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 379-390; Chem. Abs., vol. 31, 1937, p. 5135.

Water-gas reaction has been studied at 700° and 800° in the presence of Ni catalysts containing 10% each of Al_2O_3 , MgO , SiO_2 , ThO_2 , CuO , MnO , CaO , Fe_2O_3 , and ZnO . The catalyst Ni+10% MgO has the greatest activity for the oxidation of CO.

3479. Production of Carbon Monoxide and Hydrogen by Means of the Methane-Steam Reaction. II. Effect of Temperature Upon the Catalytic Activity of Nickel Catalyst for the Hydrogenation of Benzene. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 593-597; Chem. Abs., vol. 31, 1937, p. 6443.

Change of catalytic activity of the catalyst Ni+10% various oxides has been studied at the temperature range 500°-700° for the hydrogenation of benzene. It has been found that Ni+10% Al_2O_3 is most active within this temperature range.

3480. Production of Carbon Monoxide and Hydrogen by Means of the Methane-Steam Reaction. III. Action of Nickel Catalyst Upon Methane-Steam Reaction. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 610-620; Chem. Abs., vol. 31, 1937, p. 6443.

Activity of the catalyst Ni+10% various oxides has been studied for the CH_4 -steam reaction at 700° and at 800°, and the results are reviewed in comparison with those of the previous articles.

3481. Production of Carbon Monoxide and Hydrogen by Means of the Methane-Steam Reaction. IV. Nickel Sulfate as a Catalyst. Jour. Chem. Soc. Japan, vol. 58, 1937, pp. 1007-1012; Chem. Abs., vol. 32, 1938, p. 735.

3482. Production of Carbon Monoxide and Hydrogen by Means of Methane-Steam Reaction. V. Effect of Potassium Nitrate Upon the Catalytic

Activity of a Nickel Catalyst. Jour. Chem. Soc. Japan, vol. 59, 1938, pp. 29-39; Chem. Abs., vol. 32, 1938, p. 3008.

Catalytic actions of Ni and Ni+ promoter for the reactions are retarded by the presence of KNO_3 . The degree of retardation differs with different kinds of promoter.

3483. Production of Carbon Monoxide and Hydrogen by the Methane-Steam Reaction. VI. Effect of Potassium Carbonate on the Catalytic Activity of Nickel Catalysts. Jour. Chem. Soc. Japan, vol. 60, 1939, pp. 191-198; Chem. Abs., vol. 33, 1939, p. 4499.

When 3.3-33% K_2CO_3 is added to Ni catalysts, the reaction rate of CH_4 -steam reaction decreases.

3484. Researches on the Synthesis of Gasoline From Carbon Dioxide and Hydrogen at the Imperial Fuel Research Institute. Jour. Fuel Soc. Japan, vol. 16, 1937, pp. 451-496 (in English, pp. 55-60); Chem. Abs., vol. 31, 1937, p. 6837.

Many experiments were carried out with Ni and Co catalysts. The activity of a Ni and Co catalyst is increased enormously by adding a small amount of irreducible oxides, such as oxides of Al, Mn, Cr, U, and Th. The promoting action of these catalysts mainly is due to their preventing the sintering of the reduced Ni and Co at the higher reduction temperature. A number of synthetic experiments under pressure also were carried out. One of the factors accelerating the formation of solid paraffin was due mainly to the elevation of the catalyst temperature by the heat of reaction as well as the increase of added amount of the oxides of U and Th to Ni and Co catalysts.

3485. Synthesis of Gasoline From Carbon Monoxide and Hydrogen at the Imperial Fuel Research Institute. Jour. Fuel Soc. Japan, vol. 16, 1937, pp. 55-60; British Chem. Abs., 1937, B, p. 1005.

Promoting action of Th, Al, U, and Mn oxides on the activity of Co and Ni catalysts mainly is due to their preventing the sintering of the reduced Co and Ni at the higher reduction temperature. Formation of solid paraffin, which occurs when the synthesis is carried out under pressure, can be ascribed in part to raising the catalyst temperature by the heat of reaction.

3486. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. I. Catalysts Prepared by the Precipitation Method. (1). Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 435-440; Jour. Chem. Soc. Japan, vol. 59, 1938, p. 140; Chem. Zentralb., 1939, I, p. 4752; Chem. Abs., vol. 33, 1939, p. 4747.

In the synthesis of liquid hydrocarbons from CO and H_2 , the rate of the consumption of CO with a U_2O_5 catalyst containing Co 5% and Cu 12%, which need not be reduced at a high temperature, was scarcely increased owing to the addition of kieselguhr. The yield of liquid hydrocarbons increased gradually with an increase of the amount of kieselguhr. This fact shows that the proper amount of kieselguhr added to the catalyst suppresses the too violent hydrogenating power of the catalyst for production of liquid hydrocarbons and retards formation of gaseous hydrocarbons and CO.

3487. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. II. Catalysts Prepared by the Precipitation Method. (2). Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 35, 1939, pp. 441-446; Jour. Chem. Soc. Japan, vol. 59, 1938, p. 140; Chem. Zentralb., 1939, I, p. 4752; Chem. Abs., vol. 33, 1939, p. 4747.

Activities of Co catalysts, which must be reduced at high temperature, were greatly increased by adding

kieselguhr, and the depression in the activities caused by the elevation of the reduction temperature was decreased greatly by a proper amount of kieselguhr, although the optimum reduction temperature was raised with an increase of the amount added. The rates of elevation of the optimum reduction temperature for Co catalysts, with an increase of the amounts of promoter (Th, U, and Mn oxides) and carrier (kieselguhr) added, differed considerably; a small addition of promoter corresponded to the case where a larger amount of carrier was added. This fact may be attributed to a difference between the incorporated states of promoter and carrier with Co, the former being more intimately incorporated with Co than the latter. The difference between promoter and carrier is not so great.

3488. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. III. Catalysts Prepared by the Roasting Method. (1). *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, vol. 35, 1939, pp. 481-486; *Chem. Zentralb.*, 1939, II, p. 3044; *Chem. Abs.*, vol. 33, 1939, p. 6535.

Catalysts containing 5% Co and 12% Cu or 5% Co and 4% Cu, activated with U_2O_8 , are less active and have lower optimum reduction temperatures when prepared by roasting below 300° than when prepared by precipitation. More kieselguhr must be added to the roasted catalysts to obtain the activity of the precipitated material.

3489. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. IV. Catalysts Prepared by the Roasting Method. (2). *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, vol. 36, 1939, pp. 47-52; *Chem. Zentralb.*, 1939, II, p. 3044; *Chem. Abs.*, vol. 33, 1939, p. 6535.

Optimum reduction temperature for Co catalysts prepared by roasting is lower and the decrease in activity from using high reduction temperatures is greater than for precipitated Co catalysts. The amount of kieselguhr in the roasted catalysts must be increased to raise their activity. The decrease in activity of roasted Co catalysts is greatest when Mn is used as a promoter, less with heavier ThO_2 , and least with the heaviest U_2O_8 .

3490. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. V. Selection of Catalysts for the Synthesis. (1). *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, vol. 36, 1939, pp. 178-182; *Chem. Abs.*, vol. 33, 1939, p. 5934.

Ni catalysts containing 10% of various oxides were prepared by roasting the nitrates and reducing the Ni in H_2 at temperatures 300°-700°. Their activities in the hydrogenation of C_2H_4 at 190° were compared. The loss of activity resulting from elevation of the reduction temperature was least for $Ni-Al_2O_3$, followed by $Ni-ThO_2$, $Ni-SiO_2$, and $Ni-MgO$. The loss for $Ni-CuO$, $Ni-Fe_2O_3$, and $Ni-ZnO$ was less than for a Ni catalyst at 300°-550°, but greater at 550°-800°. $Ni-MnO$ and $Ni-CaO$ lost their activity rapidly as the reduction temperature increased. The activities of the Ni-metallic oxide catalysts for the synthesis of liquid hydrocarbons from CO and H_2 were only 20% of that of $Ni-10\% Al_2O_3$ catalyst at 210°.

3491. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. VI. Selection of Catalysts for the Synthesis. (2). *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, vol. 36, 1939, pp. 251-261; *Chem. Abs.*, vol. 34, 1940, p. 314.

Activity of a Ni catalyst, prepared by precipitation from nitrate solution by K_2CO_3 , followed by reduction of the oxide by H_2 , diminished more rapidly with in-

crease of temperature of reduction than that of a similar catalyst prepared by roasting. Apparently, K_2CO_3 and KNO_3 were absorbed on the active spots. A $Ni-10\% Al_2O_3-100\%$ kieselguhr catalyst prepared by the precipitation method was fairly active for the CO- H_2 synthesis but showed a high optimum reduction temperature, 450°-500°. Reduction of the proportion of Al_2O_3 to 7.5%, or substitution of about 50% of the Ni by Co, lowered the optimum reduction temperature. $Ni-10\% Al_2O_3$ and $Ni-10\% Al_2O_3-100\%$ kieselguhr catalysts prepared by precipitation were about as active as a $Ni-10\% Al_2O_3$ catalyst prepared by roasting, for the hydrogenation of C_2H_4 , but were more active for the CO- H_2 synthesis.

3492. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. VII. Activities of the Catalysts Used for the Synthesis. *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, vol. 36, 1939, pp. 262-270; *Chem. Abs.*, vol. 34, 1940, p. 314.

Addition of 0.2-0.3 gm. of $NiSO_4$ to a $Ni-10\% Al_2O_3-100\%$ kieselguhr catalyst, prepared by precipitation, containing 6 gm. of Ni, almost completely suppressed its activity for the CO- H_2 reaction, but did not greatly affect its activity for the hydrogenation of C_2H_4 , for the suppression of which 0.8-0.9 gm. of $NiSO_4$ was required. A catalyst containing 0.8-0.9 gm. of $NiSO_4$ retained its activity for the hydrogenation of nitrobenzene to aniline and of phorone to valerone, and for the water-gas reaction. When the catalysts were prepared by roasting, less $NiSO_4$ was required to suppress the activity for the hydrogenation of C_2H_4 , 0.2-0.3 gm. for Ni (6 gm.)-10% Al_2O_3 , and 0.04-0.05 gm. for Ni (6 gm.). It is inferred that the reaction of CO with H_2 is catalyzed by the most active spots, whereas the hydrogenation of C_2H_4 and the other reactions are accelerated by respectively less-active spots.

3493. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. VIII. Changes on the Catalyst Surface Caused by the Addition of Promoter and Carrier. *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, vol. 36, 1939, pp. 335-343; *Chem. Abs.*, vol. 33, 1939, p. 9103.

Tests of Ni-Cr and Ni-Cr-kieselguhr catalysts showed the optimum ratios of Cr and kieselguhr to Ni to be 7.5% and 50%, respectively. A $Ni-7.5\% Cr-50\%$ kieselguhr catalyst ($Ni-7.5\%$, $Cr-50\%$) was more active than a $Ni-10\% Al_2O_3-100\%$ kieselguhr catalyst for the reaction of CO and H_2 . For the hydrogenation of benzene, the activity varied in the opposite order. In the Ni-kieselguhr catalyst, the optimum ratio of kieselguhr to Ni was 1:2 for the CO- H_2 reaction and 50:1 for the hydrogenation of benzene. It was suggested that the action of the promoter does not differ greatly from that of the carrier, although a larger amount of the carrier is needed to prevent sintering during reduction of the catalyst.

3494. ———. Catalysts for the Synthesis of Liquid Hydrocarbons From Carbon Monoxide and Hydrogen. IX. Relation Between the Surface Dispersity of Catalysts and the Catalytic Activities. *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, vol. 36, 1939, pp. 344-351; *Chem. Abs.*, vol. 33, 1939, p. 9103.

Co-kieselguhr catalysts for the hydrogenation of benzene were prepared by 3 methods: (a) $CO(NO_2)_2$ was treated with K_2CO_3 in the presence of kieselguhr. (b) $Co(NO_2)_2$ was treated with K_2CO_3 , and the precipitate was dried and mixed with kieselguhr in a little H_2O . (c) $Co(NO_2)_2$ and kieselguhr were mixed and roasted. The products were dried and reduced by H_2 at various temperatures. The optimum ratios and reduction temperatures were determined. The activities of the catalysts prepared by these methods were in the order $2 > 1 > 3$. Optimum ratios of Co to kieselguhr were

1:10 to 1:20 for (a), and 1:40 for (b) and (c). The rate of elevation of the optimum reduction temperature with increase in kieselguhr was largest for (a) and smallest for (b). The small rate for (b) was attributed to the high degree of surface dispersity of Co on kieselguhr. Corresponding results were obtained with a $(4Ni+1Co)-7.5\% Cr$ catalyst.

3495. ———. Fischer Process—Japan. *Jour. Fuel Soc. Japan*, vol. 18, 1939, p. 47.

Work at the Imperial Fuel Research Institute is reported on Ni and Ni-Co catalysts promoted by Cr oxide. Cr oxide was found to be a superior promoter both for Ni and Ni-Co catalysts, and 175 cc. per m.³ of gasoline was obtained with a Ni-Co-Cr-kieselguhr (80:20:7.5:100) catalyst. The activity of Ni-Cr catalysts for the synthesis was larger than that of Ni-Al catalysts, but in the case of the hydrogenation of benzene, a quite contrary relation was obtained, this being attributed to the change of the active surface of the catalyst according to the addition of promoter and carrier. Synthesis experiment under pressure showed that synthesis of pure liquid hydrocarbons, containing no O, was possible even under a high pressure of about 50 atm., this being quite contrary to the results obtained by F. Fischer and collaborators. Yield of gasoline up to 125 cc. per m.³ was obtained with a Co-ThO₂-kieselguhr (100:15:100) catalyst under 40 atm.

3496. ———. Nickel Catalysts for the Conversion of Water Gas. *Jour. Chem. Soc. Japan*, vol. 60, 1939, pp. 311-318; *Chem. Abs.*, vol. 33, 1939, p. 4765.

Addition of KNO_3 to the Ni catalyst retards the formation of C_2H_4 in the water-gas reaction, $CO+H_2O \rightarrow CO+H_2$, at 400°.

3497. ———. (R. C. GRASS, Ed.) Synthesis of Hydrocarbons. Bureau of Mines Inf. Circ. 7594, 1951, 60 pp.

This paper, among the documents obtained by the United States Naval Technical Mission to Japan, gives detailed data of research on the production of synthetic liquid fuels from coal by the Fischer-Tropsch or gas-synthesis process by the Imperial Fuel Research Institute of Japan between 1932 and 1935; also contains brief reviews of research on the gas-synthesis process before 1935 in Germany, Japan, Britain, United States, and France. Summary: Studies were made of the effects of reaction temperature, gas velocity, and synthesis gas composition on the yield of liquid hydrocarbons, and an optimum reaction temperature and gas velocity were found to exist. A compromise between the most desirable yield of liquid hydrocarbons and the greatest catalyst durability was established at a $H_2:CO$ ratio of 2:1. A ratio of diatomaceous earth to the metals content of the catalyst was found to produce the best results between 1:1 and 3:4; silica gel also was found to be a fair carrier. In preparing catalysts acetates were found to be as good a source material as nitrates. Studies of Ni catalysts showed that by using 100 Ni:20 Mn:8 U_2O_8 :4 ThO_2 catalyst, 168.8 ml. of gasoline was obtained per cu. m. of synthesis gas. Co-Cu catalysts and Ni-Co-Cu catalysts were investigated. The temperature at which Co is reduced does not impair its subsequent catalytic activity in any way. The reduction temperature of Co may be lowered from 350° to 200° by adding more than 5% Cu; to lower the reduction temperature of Ni from 450° to 250°, more than 100% Co and more than 10% Cu (relative to the Ni) must be added. Studies of catalysts containing Ag showed that, although Ag is inferior to Cu as a means of lowering the reduction temperature, it is superior to Cu as a promoter. The mechanism of the hydrocarbon synthesis was discussed.

3498. TSYSKOVSKI, V. [Synthesis of Fatty Acids From Fractions of Petrolatum.] *Jour. Appl. Chem.* (U. S.

S. R.), vol. 19, 1946, pp. 428-434; U. O. P. Co. Survey Foreign Petroleum Literature Transl. 655, 1946, 7 pp.

Previous attempts to use petrolatum as a raw material for oxidation to acids to be used for the manufacture of greases were unsatisfactory because of the unsuitability of the molecular weights of a substantial proportion of the charging stock and its contents of isoparaffins. Conditions of distillation were found during which isoparaffins contained in petrolatum are for the most part broken down into straight-chain paraffins. Fractions of the material amounting to 70% can then be oxidized to obtain acids of molecular weight not exceeding 322, which are quite suitable for the preparation of calcium-base greases.

TUR, E. V. See abs. 2709.

3499. TURKEVICH, J. Electron Microscopy of Catalysts. *Jour. Chem. Phys.*, vol. 13, No. 6, 1945, pp. 235-239.

Number of electron micrographs are presented: Pt oxide, Adams Pt catalyst, platinized asbestos, the same sintered, activated alumina, active silica gel, alumina silicate cracking catalyst, Zn oxide MeOH catalyst, and a Fischer catalyst of Ni-ThO₂ supported on kieselguhr. The kieselguhr is seen to be composed of diatoms, which are particles full of holes 1,300 Å diam. These openings offer a large surface for support of the Ni and ThO₂.

See abs. 3395, 3395a.

3500. TURKEVICH, J., AND SELWOOD, P. W. Solid-Free Radical as Catalyst for Ortho-Para Hydrogen Conversion. *Jour. Am. Chem. Soc.*, vol. 63, 1941, pp. 1077-1079; *Chem. Abs.*, vol. 35, 1941, p. 3512.

Object of this investigation was to determine whether the list of solid substances catalytically active for this transformation could be extended to include solid free radicals. The organic free-radical chosen for the investigation was α, α -diphenyl- β -picrylhydrazyl (I). The magnetic characteristics of (I), the corresponding hydrazine, active ZnO and ignited ZnO were determined. H_2 adsorption at liquid-air temperature was determined on (I), active ZnO, and an intimate mixture of the 2. Ortho-para H_2 conversion at liquid-air temperature was slow on ZnO and slow on the free radical but very rapid on an intimate mixture of the 2. 3501. TURKEVICH, J., SCHESSLER, D. O., AND INSA, A. P. Study of the Interaction of Ethylene and Deuterium. *Nuclear Sci. Abs.* 4, No. 19, Oct. 15, 1950, p. 842.

Interaction of C_2H_4 and D_2 can take place by addition or exchange. These reactions are studied by mass spectrographic analysis of the various deuterio-ethylenes and deuterio-ethanes and the H_2-D_2 gas during the catalytic conversion of ethylene into ethanes. The results obtained for the interaction of ethylene with 3 vol. D₂ on a Ni wire at 90° C. show that exchange is more rapid than addition, and that the concentration of light ethylene decreases exponentially, but that of the substituted ethylene goes through a maximum before it finally reaches O. A surprising result is the discovery of completely light ethane from the reaction of ethylene and D_2 . These results suggest that the ethylene hydrogenation is effected by the H_2 that was previously on other ethylene, and only indirectly by the H_2 mol. The point is being further investigated, and the mechanism formulation is being reserved until the kinetic investigations are completed.

TURNER, G. See abs. 329.

3502. TUTIYA, H. Catalytic Decomposition of Carbon Monoxide. I. Iron as Catalyst. *Bull. Inst. Phys. Chem. Research (Tokyo)*, vol. 8, 1929, pp. 206-219; *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, vol. 10, 1929, pp. 69-82; *Chem. Abs.*, vol. 23, 1929, p. 3620.

Decomposition rate of CO was measured in presence of C, 2 kinds of Fe wire, reduced Fe, and a mixture of

Fe₂C and C, and the carbons produced were studied with X-ray. Conclusions: (1) Fe functions not as a catalyst but as a catalyst donor, that is, as a supporter of autocatalytic decomposition of CO. (2) When CO decomposes in presence of Fe, Fe₂C forms first, and the 2 reactions, $3Fe + 2CO = Fe_2C + CO$, and $2CO = C + CO$, progress concurrently. (3) Fe₂C has a remarkable catalyzing ability and plays a chief role in the decomposition of CO. (4) C isolated from the catalytic decomposition not only has no catalyzing power but even hinders the catalytic effect of Fe₂C. (5) Fe₂C becomes very densely packed with the C, which is isolated by decomposition, till it ceases completely to catalyze. On this account Fe₂C in the C is very difficult to remove. This suggests a quality of C that is obtained catalytically by decomposition in presence of metal. (6) X-carbide of U. Hofmann is Fe oxide.

3503. ———. [Catalytic Decomposition of Carbon Monoxide. II. Is the So-Called X-Carbide Really Formed in the Iron Catalyst?] Bull. Inst. Phys. Chem. Research (Tokyo), vol. 8, 1929, pp. 609-613, abs. sec. 2, pp. 76-77; Chem. Abs., vol. 24, 1930, p. 3159.

X-ray spectrometry of specimens of Fe carbide and Fe₂O₃ used as catalysts in the decomposition of CO gave no evidence of the formation of new compounds. The photographs of samples of Fe₂O₃ taken at suitable stages of the reaction showed evidence of the successive reduction to the oxides Fe₂O₃ and FeO and later to Fe₂C. It was found that almost all the lines of strong intensity, which Hofmann (abs. 1455) ascribed to the X-carbide, agreed with those of Fe₂O₃, not only in position, but also in order of intensity; one of the weak lines, which was not common to Fe₂O₃, was due to FeO, and 2 were shown by Fe₂O₃.

3504. ———. Catalytic Decomposition of Carbon Monoxide. III. Behavior of Iron Carbides. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 10, 1931, pp. 556-562, abs. 58-59 (in English); Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 16, No. 306-309, 1931; Chem. Abs., vol. 25, 1931, p. 5615.

In the catalytic decomposition of CO by Fe₂O₃ or Fe₂C, some relations between percarbide (Fe₂O₃), cementite, and free C were determined. At 270°-320° Fe₂O₃ is reduced to Fe₂C, and no FeO, Fe, or Fe₂C is found in the course of this reduction, which indicates equilibrium exists between Fe₂O₃ and Fe₂C in the solid phase and between CO and C in the gaseous phase. Reduction at 280°-320° gives a mixture of Fe₂C and Fe₂C and the amount of the latter increases with rise in reaction temperature. At 450° Fe₂C decomposes rapidly into Fe₂C and C. At 270°, Fe₂C is formed not only from Fe and its oxides but from Fe₂C.

3505. ———. Catalytic Decomposition of Carbon Monoxide. IV. Behavior of Nickel Carbides. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 10, 1931, pp. 951-973, abs. 83-84; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 16, No. 328-329, 1931; Chem. Zentrbl., 1932, I, pp. 782-783; Chem. Abs., vol. 27, 1933, p. 1809.

An X-ray investigation of the catalytic decomposition of CO by Ni or NiO has confirmed the formation of Ni₂C and a percarbide, Ni₂C. The percarbide is formed from NiO at 270° and rapidly decomposes into Ni₂C and C at 284°; it also is decomposed by atmospheric H₂O vapor. Ni₂C is quite stable at 285° and catalyzes the decomposition of CO. In the temperature range of stability of Ni₂C, the reaction $3Ni + 2CO = Ni_2C + CO$ is possible, but not reaction $2CO = C + CO$. Free Ni is found in the earlier stages of reduction of NiO, but later changes completely to carbides.

3506. ———. Catalytic Decomposition of Carbon Monoxide. V. Behavior of Molybdenum Carbides. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 11,

1932, pp. 1136-1149; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 19, No. 384-392, 1932; Chem. Abs., vol. 27, 1933, p. 1809.

CO was decomposed under various conditions in presence of metallic Mo, its carbides or solid solution of Mo₂C, and solid phases formed of carbides and C were examined by the X-ray method. Mo₂C is formed at 450°-600°; a very diffused diffraction line of C (002) is observed in the powder spectrogram of the reaction product at 600°. Mo and its carbides are not oxidized in CO at 450°-800°; CO flowing over the mixture of Mo₂C and C is decomposed at 600°. C itself having no catalytic property. A new carbide phase, most probably Mo₂C, is formed at 750°. At 750°-800° the mixture of Mo₂C, Mo₂C, and C is formed, and CO is decomposed without the existence of metallic Mo; the reaction product at 650°-700° contains, besides Mo₂C, a metastable carbide phase.

3507. ———. X-Ray Observation of Molybdenum Carbides Formed at Low Temperatures. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 11, 1932, pp. 1150-1156; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 19, No. 384-392, 1932; Chem. Abs., vol. 27, 1933, p. 216.

Mo atoms in Mo₂C have the dense hexagonal lattice, 1 atom being in the position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and another in $(\frac{1}{2}, \frac{1}{2}, 0)$. The C atom in the cell containing 1 mol. is perhaps in the position (0 0 0). Lattice constants are: $a = 2.994 \text{ \AA. U.}$, $c = 4.722 \text{ \AA. U.}$, $c/a = 1.577$. The atoms of C and Mo in the unit cell of Mo₂C have the following coordinates, respectively: C $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, Mo (0 0 0); the lattice constants are: $a = 2.901 \text{ \AA. U.}$, $c = 2.786 \text{ \AA. U.}$, $c/a = 0.960$, and, thus, the C atom in Mo₂C has a radius of 0.785 \AA. U. No clear distinction between the lattice constants of Mo₂C and of the metastable carbide phase was found; the reflections from the 2 carbides differ markedly in their relative intensities.

3508. TUTTLE, R. B. Two New Coal-to-Oil Plants Are Demonstrated by Mines Bureau. Oil Gas Jour., vol. 48, No. 1, 1940, pp. 58, 150.

Brief description of plants and operation of the coal-hydrogenation and the gas-synthesis units recently dedicated at Louisiana, Mo. The first is designed to operate at a pressure of 10,300 p. s. i. and temperature of 600°-900° F. and produce 200-300 bbl. of products per day. The actual production capacity is dependent on the coal and catalyst used. The gas synthesis unit is a designed modification of the Fischer-Tropsch process, and has a nominal rating of 80-100 bbl. of product per day, comprising 5-10 bbl. of propane, 55 bbl. gasoline, 10 bbl. diesel fuel, and 12 bbl. heavy oils and waxes. Two new-type Bureau-developed converters are to be used for the conversion of gas to liquid fuels. Each has a different cooling system: The first unit is cooled by circulating oil through a fixed bed of granular catalysts, the 2d by passing the gas through a rapidly circulating slurry of coolant oil and powdered catalyst. O₂ for processing operations is produced by a Linde-Frankl generator at temperatures of more than 300° F. below 0°. The synthesis gas is produced by O₂ steam gasification of pulverized coal at a temperature of 2,000° F. or more.

3509. TWIGG, G. H. Catalytic Isomerization of 1-Butene. Proc. Roy. Soc. (London), vol. 173, 1941, A, pp. 106-117; Chem. Abs., vol. 35, 1941, p. 5775.

Early work upon the isomerization of 1-butene to 2-butene on a Ni catalyst in the presence of H₂ is extended to D₂. The double-bond migration is examined simultaneously with the exchange and hydrogenation reactions. At 65°, the kinetics of double-bond migration are identical with those of hydrogenation, the rate of the reaction being proportional to the square

root of the pressure of the butene or H₂. The energies of activation are found for the temperature range 70°-126°. At the lowest temperature, the rate of double-bond migration is 6 times that of exchange. This is in agreement with the theory that the catalytic exchange between the olefins and D₂ takes place through the formation of an associative complex. The step that determines the rate in the double-bond migration is the 2d fast step of the exchange reaction. The accounts given for the double-bond migration by the dissociative theory of exchange must be regarded as inadequate; whereas the associative theory succeeds in giving a consistent picture of the whole reaction process.

3510. TWIGG, G. H., AND RIDEAL, E. K. Chemisorption of Olefins on Nickel. Trans. Faraday Soc., vol. 36, 1940, pp. 533-537; Chem. Abs., vol. 34, 1940, p. 4634. Calculations were made that show that the previous view regarding the mode of adsorption is possible with very little distortion of the adsorbed molecule; namely, that olefins are chemisorbed on Ni with opening of the

double bonds and adsorption on 2 Ni atoms. The interatomic spacing of the catalyst atoms is the important factor where 2-point contact is required in adsorption. There is little interaction between neighboring adsorbed ethylene molecules; for the higher olefins, however, the interaction is considerable, and these molecules cannot cover the whole surface.

3511. TYLER, F. Magnetization-Temperature Curves of Iron, Cobalt, and Nickel. Phil. Mag., vol. 11, No. 7, 1931, pp. 596-602; Chem. Abs., vol. 25, 1931, p. 2609.

Curves for σ/α , against T/θ are almost identical for Fe, Co, and Ni. They are definitely incompatible with the classical curve and with quantum curves for f greater than, or equal to, 1. There is close agreement when $f = \frac{1}{2}$. The electron spin is to be regarded as the fundamental magnetic element operative for Ni, Fe, and Co. The value of $f = \frac{1}{2}$ means that electron spins are independent and that there is a tan h distribution. The electrons are not free but associated with ions as in Heisenberg's theory.

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3512. UBBELOHDE, L. [Anthracite in German Motor-Fuel Economy.] Oel u. Kohle Erdoel Teer, vol. 12, 1936, pp. 333-359.

Various processes for motor-fuel production from coal are discussed: Coking, distillation, hydrogenation, Fischer-Tropsch, Pott and Broche, and Uhde.

3513. ———. [Mineral-Oil Research.] Oel u. Kohle Erdoel Teer, vol. 12, 1936, pp. 983-988; Chem. Abs., vol. 31, 1937, p. 3247.

An up-to-date account of processes for obtaining motor fuels and oils from materials other than petroleum, such as from coal and lignite by distillation, hydrogenation, Fischer-Tropsch, Pott-Broche.

UHL, W. C. See abs. 268.

ULLICH, H. See abs. 3147.

ULLMANN, D. See abs. 1954.

3514. ULLRICH, A. [Most Recent Processes for the Catalytic Production of Methanol from Carbon Monoxide and Hydrogen.] Metallbörse, vol. 19, 1929, pp. 1181-1182, 1238-1239, 1294-1295; Chem. Abs., vol. 23, 1929, p. 3898.

Review.

3515. ———. [Preparation of Methyl Ether From Oxides of Carbon by Means of Catalytic Hydrogenation.] Metallbörse, vol. 19, 1929, pp. 1741-1742; Chem. Abs., vol. 23, 1929, p. 5158.

Review.

UMEMURA, T. See abs. 1900, 1901, 1902.

3516. UMINO, S. Specific Heat of Iron-Carbon System at High Temperatures, and the Heat Changes Accompanying Those in Phase. Sci. Repts. Tôhoku Imp. Univ., 1st ser., vol. 23, 1935, pp. 665-793; Chem. Abs., vol. 29, 1935, p. 4253.

Heat content of 19 Fe-C alloys containing 0.07-5.07% C was measured at numerous high temperatures up to and beyond the melting point. Electrolytic Fe and sugar C were used in preparing the melts. The heat of fusion of the δ -alloy containing 0.03% C is 65.31 cal.; 0.07% C, 64.90 cal.; of the γ -alloy containing 0.13% C, 67.19 cal.; 1.70% C, 57.8 cal. The heat of fusion of the eutectic is 60.91 cal. That of cementite, by extrapolation, is 65.0 cal., its melting point being estimated to be 1,600°. The heats of transformation of the α - into the γ -Fe at the A₁ point are calculated to be 5.59 cal. for pure Fe and 16.60 cal. for the eutectoid at 720°. The heat of solution of Fe₂C in γ -Fe of 0.90% C is 11.15 cal. at 720°; it decreases with rise in temperature and C concentration. The heat of the A₂ transformation of Fe₂C is estimated to be 9.35 cal.

3517. UNDERWOOD, A. J. V. Oil From Coal. Chem. and Ind., 1938, pp. 360-364; Chem. Abs., vol. 32, 1938, p. 4308.

Review covering carbonization, hydrogenation, gas synthesis, and liquefaction.

3518. ———. Oil From Coal. Fuel Econ. Rev., vol. 17, 1938, pp. 14, 16-21, 31; Chem. Abs., vol. 33, 1939, p. 1122.

Reviews developments during 1937 in connection with the Fischer-Tropsch process, coal hydrogenation, and the recovery of benzol from coal gas.

3519. ———. Utilization of Oil Shales and Cannel Coals in Connection With Production of Synthetic Oils. Inst. Petrol. Conf., June 1938, pp. 468-473; Chem. Abs., vol. 33, 1939, p. 3571.

Possibilities of combining the carbonization of oil shales and cannel coals with processes for the production of synthetic oils by the Bergius or Fischer-Tropsch processes are discussed. An outline is given of various schemes in which the solid residue from the carbonization of cannel coal is utilized for these synthetic processes, and the scale of operation that would probably be necessary is indicated.

3520. ———. Industrial Synthesis of Hydrocarbons From Hydrogen and Carbon Monoxide. Ind. Eng. Chem., vol. 32, 1940, pp. 449-454; British Chem. Abs., 1940, B, p. 427; Chem. Abs., vol. 34, 1940, p. 3045.

Hydrocarbons in about 70% yield are obtained from 2 H₂+CO using a Co catalyst-kieselguhr at 190°-200°, 5-15 atm.; yields are decreased and catalyst is impaired at higher pressures. A main controlling factor is the rate of removal of the products of reaction from the catalyst. Removal of wax from the surface of the catalyst maintains its activity. Various raw materials and processes for making synthesis gas are given. Conversion of CH₄ into synthesis gas (H₂:CO=2:1) by the process: $3CH_4 + CO + 2H_2O = 4CO + 8H_2$, is discussed. Accurate temperature control is necessary, and indirect watercooling is used. S is removed by passing the gas over an alkaline Fe oxide or Ni catalyst at 177°-299°. Commercial plant is described. Straight-chain hydrocarbons with gasoline fraction of low octane number, a Diesel oil fraction with high octane number, and waxes (for example, those of m. p. 90.6°) are obtained.

I. G. Farbenindustrie A.-G. Works at Leuna. XVI. Mersol Process. See abs. 1480.

3521. UNITED STATES ARMY ENGINEER CORPS. Survey of Southeastern Montana for Arenas Suitable for

Synthetic Liquid Fuel Plants. Summary of Report to Bureau of Mines, December 1943, 4 pp.

Survey showed that there are enough minable coal reserves and water supplies to support some 362 10,000-bbl.-per-day strips for a 40-yr. period, and there is enough low-cost plant coal to operate 15 such plants for 20 yr. The North Central States would be the nearest and most logical potential market area for any liquid fuels produced. The comparative costs of liquid fuel, not including processing, based on the gas-synthesis process and on the most desirable and largest area, are calculated at \$1.80-\$2.37 per bbl. The mining cost alone is calculated at \$2.77-\$3.28 per ton of coal.

3522. Survey of Western Kentucky, Northwestern Colorado, and Southeastern Texas for Areas Suitable for Synthetic Liquid Fuel Plants. Summary of Report to Bureau of Mines, December 1943.

Sample surveys of 4 States have indicated that they alone have enough coal, shale, and natural gas to produce 9,000,000-10,000,000 bbl. of synthetic liquid fuels for 40 yr. Western Kentucky has coal reserves of 16,768 million tons or enough to meet the requirements of either 138 10,000-bbl.-per-day synthetic plants or 164 hydrogenation plants of the same size. Water supplies are adequate, and the area is favorably situated with respect to markets. Northwestern Colorado has coal reserves yielding 25 gal. or more per ton of easily minable coal, which will support 105 10,000-bbl.-per-day synthetic plants for 40 yr., together with available coal reserves adequate to supply 279 synthetic plants or 336 hydrogenation plants. Water supplies available by 1963 for all new uses would limit the synthetic-fuel capacity to 1,050,000 bbl. per day from shale, plus 510,000-\$40,000 bbl. per day from coal, depending on the process used. Southeastern Texas has an estimated 9.5 trillion cu. ft. of natural gas, enough to support 15 10,000-bbl.-per-day synthetic plants for 20 yr. Its availability, however, depends on economic and conservation considerations, which could very definitely limit the consumption.

3522a. Synthetic Liquid Fuel Potential of the United States. Report for the Bureau of Mines, March 3, 1952. Chem. Eng. News, vol. 30, 1952, p. 2,101.

Report based on a survey of the United States and Alaska by Ford, Bacon and Davis, Inc. to the Army Corps of Engineers. The survey reveals that there are sufficient available supplies of coal, oil shale, and natural gas in suitable general areas in 25 States to produce 226.4 billion bbl. of synthetic liquid fuels by the hydrogenation of coal, or 195.3 billion bbl. by the synthetic (Fischer-Tropsch) process. An additional 731.1 million bbl. of liquid fuels could be obtained from natural gas by the Fischer-Tropsch method, while 99.4 billion bbl. are obtainable by retorting oil shale. In other words, available coal supplies could yield 15.5 million bbl. of liquid fuels per day by hydrogenation or 13.4 million bbl. per day by the synthetic process, plus 6.8 million bbl. per day by retorting oil shale, for a period of 40 yr. Natural gas could add 107,000 bbl. per day by the synthetic process for 20 yr. Plant sizes adapted are 10,000 bbl. of synthetic liquid fuels per day for coal hydrogenation, Fischer-Tropsch process for coal, and retorting of oil shale; and 5,000 bbl. per day of natural gas for the Fischer-Tropsch plant for natural gas. The report indicates that there are 37 States with significant resources of these 3 raw materials plus oil-impregnated material. The following factors were considered

in selecting suitable areas: H₂O supply, power, access transportation, labor, housing, marketing and products transportation, waste disposal, plant investment, processing costs and strategic considerations. Only those areas with respect to coal were selected which had 60 million ton of recoverable coal in a 3-mile radius. The coal must have a minimum calorific value of 4,500 B. t. u. per lb. Other limitations included thickness of beds and depth of overburden. Because of these limitations, the suitable areas include only about 10% of the minable coal as estimated by the Federal Geological Survey. Basic criteria for oil shale were the existence of 200 million ton in a 5-square-mile area. The primary shale also must yield 25 gal. of oil per ton with 15 gal. per ton for the secondary shale. Bed thickness was limited to 25 ft. or more. The natural gas minimum requirements were 225 trillion B. t. u. in a 40-mile radius (primary) and 225 trillion B. t. u. (secondary). The gas in a 20-mile radius must have a minimum calorific content of 700 B. t. u. per ft.³ and that in the 40-mile radius must have a content of 400 B. t. u. per ft.³ The report also covers estimated costs of plants, manufacturing, and coal production. It also includes a large number of charts and tables.

3523. UNITED STATES BUREAU OF MINES. Production of Synthesis Gas From Wyoming Subbituminous Coal. General Investigation of Methods and Flowsheet for Plant to Process 8,000,000 Cubic Feet per Day. Special Report, November 1946, 23 pp.

To obtain general information on the advantages and disadvantages of various methods of producing synthesis gas from a coal like the Wyoming coal, 4 methods are considered suitable for treating this coal, and calculations are made of the investment and production costs for a plant with a capacity of 100,000 N m.³ per hr. of synthesis gas. The high content of H₂ of Wyoming coal promises very high tar content and, consequently, very favorable conditions for utilizing it for the production of motor fuels by combining carbonization and byproduct gasification with the synthesis of hydrocarbons and hydrogenation of tar. The 4 methods investigated are: Lurgi pressure gasification; combined carbonization-gasification with O₂ and with burning of coke and cracking of carbonization gas; the same with use of air in the 1st step and O₂ in the 2d with burning of the carbonization gas and gasification of the coke; and the Koppers complete gasification of powdered coal. Cost of equipment is taken from figures available from German sources. Corresponding figures for the United States are calculated with the ratio of 1 RM.:\$0.50 for the investment cost and 1 RM.:\$1.00 for the cost of labor, with a rough adjustment for special work.

Further calculations on 3 so-called pioneer plants A, B, and C: Carbonization-gas producer plant; Koppers pulverized-coal gasification; and Lurgi pressure gasification give production costs per 1,000 N m.³ on the basis of capacities of 8,000,000 cu. ft. of ideal gas per day and 320 operating days, respectively, of \$9.30, \$11.80, and \$11.50. Here again the combined carbonization-gasification method is found to be the most favorable one. It is proposed to erect 2 units of the carbonization-gasification type with the necessary equipment for operating each of the units for the production of gas as well as for the carbonization of coal and the production of coke, as this seems the safest, cheapest, and most-flexible method with respect to the requirements of a pilot-experimental plant, which should be able to handle various types of coal from such standpoints as tar recovery and alteration of the CO:H₂ ratio. It might also prove an economical method for the treatment of oil shales with more than 10% of oil.

Investment costs and production figures for 100,000 N m.³ per hour of synthesis gas

	I Gasification of pulverized coal (Koppers)		II Lurgi pressure gasification		III Carbonization with O ₂ ; gasifica- tion with O ₂		IV Carbonization with air; gasifica- tion with O ₂	
Investment cost:	49.5	24.75	54.0	27.0	50.2	25.1	46.6	23.3
Million RM.								
Million dollars.	740,000	420	945,000	600	995,000	550	925,000	450
Coal consumption, tons per year								
Wages:	1.05	1.05	1.5	1.5	1.37	1.37	1.13	1.18
Million RM.								
Million dollars.	11.0	20	13.5	24.5	12.8	23.4	11.5	21.5
Percent of production cost.								
Production cost per year:	9.6	5.18	11.14	6.13	10.66	5.81	9.70	5.27
Million RM.								
Million dollars.			44,200		65,500		60,500	
Tar production, tons per year								
Value of tar:			4.86	1.33	6.58	1.65	6.05	1.51
Million RM.								
Million dollars.			43.5	21.6	62.0	23.3	62.0	28.5
Percent of production cost.								
Production cost, 1,000 N cu. ft.	10.9		7.2	5.40	4.60	4.70	4.24	4.25
Million RM.								
Million dollars.			5.9					

3524. UNITED STATES BUREAU OF SHIPS, NAVY DEPARTMENT. Bibliography of Synthetic Liquid Fuels. Bib. 35, Apr. 2, 1945, 65 pp.; PB 1752.

Subject list of articles compiled for the Special Fuels Section of the Research and Standards Branch in connection with investigations of synthetic liquid fuels from oil shale, low-temperature carbonization of coal, Fischer-Tropsch synthesis, and Bergius high-pressure liquefaction of coal.

3525. UNITED STATES CONGRESSIONAL COMMISSION ON PUBLIC LANDS AND SURVEYS. Synthetic Liquid Fuels. 1944, 469 pp.

3526. UNITED STATES INDUSTRIAL CHEMICALS, INC. American Hydrocarbon Synthesis. U. S. Industrial Chemical News, I-XII, January-December 1948; Chem. and Eng. News, vol. 26, 1948, adv. sec., pp. 153, 391, 683, 1057, 1341, 1757, 2059, 2343, 2747, 3035, 3331, 3611.

Series of articles deals with various aspects of the chemical development of products of the Fischer-Tropsch synthesis to be manufactured by Hydrocol, Inc. at its Texas plant following the entrance of the United States Industrial Chemicals, Inc., into the field of marketing.

3527. UNITED STATES NAVAL TECHNICAL MISSION IN EUROPE. Thoria-Alumina Catalyst for Isoparaffin Synthesis. Tech. Rept., 110-45, 1945, 8 pp.; Oil Gas Jour., vol. 44, No. 37, 1946, pp. 86, 89; CIOs Rept., XXV-2; PB 289, 890.

Digest of the report, Wartime Research on Synthetic Fuels by the Kaiser Wilhelm Institut für Kohlenforschung. A catalyst of ThO₂-Al₂O₃ (1:4) gives the best yields of all catalysts investigated. Higher gas velocities may be used, the tendency for alcohol formation is low but high for C deposition. Increasing the Al₂O₃ content increases CH₄ formation, and addition of 0.5-1% K₂CO₃ raises the yield slightly. ZnO-Al₂O₃ catalyst shows slightly lower yields but better commercial prospects. Both catalysts are prepared by precipitation from the respective nitrate solution by means of Na₂CO₃. For synthesizing isoparaffins, pressures of 300 atm. and temperatures of 420°-450° are best. Yield drops rapidly below 300 atm., but, as pressures increase above this, the % of O-containing products increases until at 1,000 atm. the entire product is dimethyl ether. Temperatures below 450° show increases of alcohol and unsaturates and a decrease in C deposition. Above 450°, the reaction rate increases rapidly with mainly naphthenic products and excessive C deposition. The best synthesis gas is CO:H₂=1.2:1 and the best gas

velocity 10 l. per hr. per 20 cc. of catalyst. Operating with a ZnO-Al₂O₃ catalyst (1:4) with a CO:H₂ ratio of 1 at 300 atm. and 450°, the yields per m.³ of gas were: Total yield C₂ and higher 120-130 gm.; C₁ (90% isobutane) 50-80 gm.; C₃+ (97% iso-) 30-60 gm.

3528. Methane Cracking by Partial Combustion With Oxygen or Air in Germany. Bib. Sci. Ind. Repts., vol. 6, No. 12, 1947, p. 1050; PB 23,076-S, November 1945.

Descriptive list of 12 documents extending the subject matter of the original report by Lyon and Crawford (abs. 2155).

3529. UNITED STATES NAVAL TECHNICAL MISSION TO JAPAN. Japanese Fuels and Lubricants. Article 7. Progress in the Synthesis of Liquid Fuels From Coal. X-38(N)-7, February 1946, 333 pp.; PB 58,701; BIOS Final Rept., 1305; PB 79,230; Fuel Abs., vol. 5, 1949, abs. 237; TOM Reel 232.

This report, containing more than 30 separate papers, summarizes the findings of the Petroleum Section of the U. S. Naval Technical Mission to Japan relative to research and industrial development in the fields of high-pressure hydrogenation, Fischer-Tropsch synthesis, and low-temperature carbonization. A general history (pp. 9-22, 321-326) of the synthetic fuels program in Japan also is presented. Numerous flowsheets, charts, and tables explain the extent and nature of the developments. It is revealed that Japan, in its acute need for oil, plunged into industrial coal hydrogenation without acquiring an adequate background of experience with the intermediate-scale equipment. Also materials, particularly heat-resistant alloy steels, were not available for the construction of suitable equipment, and manufacturing facilities did not exist for fabricating reaction vessels of proper size. All evidence indicates that only 2 commercial-scale coal-hydrogenation plants were installed in Japan, and it may reasonably be interpreted that they did not have a perfected process. Also, according to information obtained, only 5 Fischer-Tropsch plants were ever put under construction; of these, only 3 were placed in operation, the 2 others being under construction at the end of the war. The Japanese 7-Year Plan called for production of 2,000,000 kl. of liquid fuels from coal by 1943, but actual production in the peak year 1944 was only 113,000 kl.

3530. Japanese Fuels and Lubricants. Article 7. Progress in the Synthesis of Liquid Fuels from Coal. Location and Output of Japanese Synthetic Oil Plants. X-38(N)-7, February 1946, pp. 14-19, 23; PB 58,701.

Company	Location	Designed capacity	Type of operation	Catalyst	Actual fuel output, kl.					
					1941	1942	1943	1944	1945	
Coal hydrogenation:										
1. Manshu Jinzo Sekiyu Co., Fushun Works.	Fushun, Manchuria.	2.5 ton/hr.; 10,000 tons per year; nominal throughout, Oyama coal.	Liquid-phase, 200 atm. 430°; vapor phase, 200 atm., 430° and 440°. 1st and 2d stage, respectively; coal:vehicle=2:3 by weight.	Liquid phase—precipitated FeS; vapor phase—40% MoS ₃ +60% acid clay; FeO; Fe ₂ O ₃ ; S; Sn(OH) ₂ ; 100:17:1; ZnCl ₂ .2H ₂ O; MoO ₃ .Sn(OH) ₂ ; Sz No. 1		770		690		
2. Chosen Jinzo Sekyu Co., Agochi Works.	Agochi, Korea.	5 tons per hr., 50,000 tons per yr.; Agochi brown coal; nominal production 10,000 kl. heavy oil.	200-250 atm.; Unable to function as coal-hydrogenation unit; Converted to MeOH synthesis.							
Total coal-hydrogenation oil						770		690		
Fischer-Tropsch:										
1. Nippon Jinzo Sekyu Co., Miike works.	Omuta, Kyushu.	30,000 tons per yr. oil output; 1,000 m. ³ /hr. converter-gas throughput.	Actual production, 16,000 tons; Ruhrchemie license 56 converters; atmospheric pressure, 180°-200°, 2-stage; actual throughput gas, 750 m. ³ . Atmospheric pressure; 24 double-tube Ruhrchemie-type converters.	Co:ThO:MgO:kieselguhr=21.2:1.2:2.4:75.2; Catalyst life, 120 days.	7,200	9,290	13,870	11,070	1,720	
2. Amagasaki works.	Amagasaki, Honshu.	30,000 tons per yr.	Atmospheric pressure; 24 double-tube Ruhrchemie-type converters.	Co			200	130		
3. Takikawa works.	Takikawa, Hokkaido.	50,000 tons per yr.	10 atm. pressure; 36 double-tube, 24 single Ruhrchemie-type converters; 4 Japanese design.	Co and precipitated Fe catalyst and natural Fe catalyst.		1,550	1,600	6,610	2,460	
4. Manshu Jinzo Sekiyu Co., Chielin works.	Chielin, Manchuria.	1,000 kl. per yr.								Under construction.
5. Chinchu works.	Chinchu, Manchuria.	40,000 kl. per yr.								Under construction.
Total Fischer-Tropsch oil					7,200	10,840	15,670	17,910	4,200	

3531. Report on Research on the Fischer-Tropsch Process at the Kyoto Imperial University. X-38 (N)-7, encl. (D), 1946, pp. 227-248; PB 58,701. Summarizes technical information pertaining to research on the Fischer-Tropsch process by Prof. G. Kita and staff at the Kyoto Imperial University. Serves only to outline the scope of the work and to present certain significant points covered in the interviews with Prof. Kita, Prof. S. Kodama, and Prof. K. Tarama. The report deals briefly with the history of the work, normal and middle pressure catalyst studies, and catalyst preparation and presents a list of papers, published for the greater part in the Journal of the Institute of Physical and Chemical Research, and a list of about 20 Japanese patents relating to the Fischer-Tropsch process.

3532. Research Activities of the Imperial Fuel Research Institute, Kawaguchi. VII. Fischer-Tropsch Process. X-38 (N)-7, encl. (E), 1946, pp. 258-262; PB 58,701. Key man in the organization was S. Tsutsumi, 1933-39. The plant ceased operation in 1940 when the plant at Miike was begun. The plant never attained more than 30% of design capacity, which was 200 kg. of total crude-oil product daily. Failure was due to poor catalysts and to faulty and cumbersome converter design. Only Ni catalysts were used, and the one giving the best results had the approximate weight composition Ni:Co:Cr:kieselguhr=40:10:7.5:50. It was prepared by precipitation from the nitrates and reduced at atmospheric pressure with H₂. Flow-sheet of the plant is shown.

3533. Report on Miike Synthetic Oil Co., Omuta, Kyushu. X-38 (N)-7, encl. (G), 1946, pp. 283-305; PB 58,701.

Miike plant was constructed in 1936-40. It utilizes the conventional low-pressure Fischer-Tropsch process with Co-ThO₂ catalyst. Synthesis gas (H₂:CO=2:1) is obtained by blending water gas and reformed coke-oven gas. The process is licensed by Ruhrchemie and most equipment was constructed by Koppers. Plant capacity was rated at 30,000 tons of product per yr., but actual production during the peak year 1943 was only 16,000 tons. This primarily was due to decreased production of synthesis gas from the high-S, low-melting-pint-ash Miike coal and to the low yield of oil per unit of synthesis gas because of low catalyst activity. Details on the history, organization, process flow sheets, plant layout, product quality, and output are presented. Fuels Act covering calendar year 1945. A progress report on the Synthetic Liquid Fuels in the United States. Rept. on the Synthetic Liquid Fuels Act, 1945, 44 pp.; Fuel, vol. 25, 1946, pp. 134-137. Comprehensive summary of the Report of the United States Secretary of the Interior on the Synthetic Liquid Fuels Act covering calendar year 1945. A progress report on the investigations already made in the fields of coal hydrogenation, liquid fuels from water gas by the Fischer-Tropsch synthesis, synthesis-gas production, oil-shale research, and the production of fuels from agricultural residues.

3535. UNITED STATES SENATE COMMITTEE ON PUBLIC LANDS AND SURVEYS. Synthetic Liquid Fuels. Hearings Before a Subcommittee, 78th Cong., 1st sess., on S. 1243, Washington, 1944, 469 pp. Reports of testimony and hearings of the Senate Committee on the possibilities of producing synthetic liquid fuels in the United States by the hydrogenation of coal and water gas.

URJOHN, T. E. See abs. 1460.

3536. URAZOVSKII, S. S. AND YAKIMKIN, N. A. [Reactivity of Gaseous Nickel Carbonyl.] Ukrain. Khim. Zhur., vol. 10, 1935, pp. 44-50; Chem. Abs., vol. 30, 1936, p. 2476. Reactions CO+3H₂→CH₄+H₂O and 2CO→CO₂+C are more powerfully catalyzed by Ni(CO)₄ at its decomposition temperature (150°) than by other Ni catalysts. The reaction CO+CH₄→MeCHO is not catalyzed by Ni(CO)₄.

3537. UREN, L. C. Impact of Wartime Conditions on the Petroleum-Producing Industry. Petrol. Eng., vol. 17, No. 4, 1946, pp. 203, 204, 206. Discussion of technologic developments during the war period and their effect on the petroleum industry. One of the most notable is the large-scale production of synthetic oil products from natural gas, coal, and shale oil. The Fischer-Tropsch process for synthesis of hydrocarbons from CO and H₂ is particularly promising and is said to be successful in producing motor fuels from natural gas at costs competitive with present day costs of petroleum fuels. Natural-gas reserves have assumed new significance as a result of this development. Hydrogenation of coal also has advanced economically and technologically.

3538. USACHEV, P. V. [Conference on Heterogeneous Catalysis, Moscow, May 13-16, 1940. Mechanism of the Catalytic Synthesis of Ammonia.] Jour. Phys. Chem. (U. S. S. R.), vol. 14, 1940, pp. 1246-1249; Chem. Abs., vol. 35, 1941, p. 3882. Addition of 7% Al₂O₃ to an Fe catalyst gives optimum results.

3539. UTILIZATION. Synthetic Liquid Fuels From Coal. Vol. 1, December 1947, pp. 37-41. Review.

3540. VALLETTE, F. [Synthetic Methanol.] Chim. et ind., Special No., April 1923, pp. 235-238; Chem. Abs., vol. 22, 1923, p. 4461. Theoretical discussion of the possibilities of the synthesis of MeOH from CO and H₂, from which it is concluded that the experience gained in the synthesis of NH₃ would enable the production of MeOH, independently of the manufacture of synthetic NH₃, to be readily established, that the cost would be approximately 1.18 francs per l., that the cost of MeOH equivalent to 1 l. of gasoline would be about 1.77 francs, and that it would be feasible to produce enough MeOH to replace the whole of the gasoline now being imported into France.

3541. [Synthetic Products Derived From Béthune Coals.] Rev. ind. minérale. No. 302, 1933, pp. 290-305. Production of MeOH from water gas by the catalytic method developed by the Mines de Béthune is discussed briefly. Describes special apparatus.

3542. [Hydrogenation of Coal.] Bull. soc. encour. ind. nat., vol. 135, 1936, pp. 353-365; British Chem. Abs., 1936, B, p. 965. Describes plant at Béthune and compares Bergius and Fischer-Tropsch processes.

3543. VALOTA, G. [Industrial Production of Gas Mixtures for Large-Scale Chemical Syntheses.] Industria (Milan), vol. 56, 1942, pp. 191-193; Chem. Zentralb., 1943, II, p. 1036; Oel u. Kohle, vol. 40, S. 5, 1944; Chem. Abs., vol. 38, 1944, p. 6520. Review of the various systems for the production of H₂-N₂ and H₂-CO mixtures by the water-gas process for use in the synthesis of NH₃, MeOH, and fuels. The production of gas for use in syntheses from gas mixtures such as coke-oven gas or natural gas is discussed.

VAN ARSDELL, P. J. See abs. 775.

VAN BAVEL, T. See abs. 1739.

VAN DINGENEX, W. See abs. 3547, 3548.

3544. VAN DYKE, B. H. Low-Pressure Oxygen Cycle. Chem. Eng. Progress, vol. 44, No. 10, 1948, pp. 20, 38, 42 (News Sec.); Chem. and Ind., vol. 63, No. 4, 1948, pp. 604-607; Petrol. Refiner, vol. 27, No. 10, 1948, pp. 540-544; Blast Furnace Steel Plant, vol. 30, 1948, pp. 1212-1215. Elliott Co. plant, described by the help of a simplified flow diagram, is designed to produce approximately 114 tons per day of 95% purity gaseous O₂, plus approximately 6 tons per day of 99.5% high-purity gaseous O₂, plus 332 tons per day of 99.5% purity dry N₂. The recovery of O₂ from the air charged to the plant is approximately 97.5%.

3545. VAN ISTERBEEK, A. [Relation Between Adsorption and the Catalytic Activity of Metals.] Mededeel. Koninkl. Vlaam. Acad. Wetenschap., Belg., Klasse Wetenschap., vol. 3, No. 10, 1941, pp. 3-20; Chem. Zentralb., 1942, II, p. 742; Chem. Abs., vol. 37, 1943, p. 4958. On the very pure Ni film the adsorption of H₂ and CO at temperatures up to 500° and pressures below 1 mm. was studied with the help of a thermal-conductivity gage. At ordinary temperature, activated adsorption of H₂ occurs; at higher temperatures, this increases and is apparently not to be attributed to diffusion adsorption. Comparison of the H₂ and CO isobars shows that at 167° and 329° the ratio of H₂:CO is 3:1 and at 2° other temperatures the ratio is 2:1, corresponding, respectively, to the synthesis of CH₄ and benzene. It is concluded that the occurrence of this stoichiometric surface ratio is related to the surface reaction. On a copper film, neither H₂ nor CO is adsorbed until a small quantity of Ni is electrodeposited. In this instance also, temperatures exist at which the H₂:CO ratio is 3:1 and also those in which it is 2:1.

3546. [Prospects of the Problem of Synthetic Oils in Belgium.] Techn. Wetenschap., Tijdschr., vol. 11, 1942, pp. 37-44; Chem. Zentralb., 1942, I, p. 2955; Chem. Abs., vol. 37, 1943, p. 3586. Discussion of future possibilities of oil synthesis in Belgium includes a review of synthetic oils, Bergius and Fischer-Tropsch processes, catalysis as the basis of the oil synthesis, relationships between catalysis and adsorption, recent determinations of adsorption at extremely low pressures and extremely pure adsorbing surfaces of Ni, Cu, and Cu activated with ThO₂ (carried out in the Laboratory of Natural History at Louvain), comparison of the results obtained with the velocity of reaction of the gas mixture CO-H₂, discussion of the regions of reaction for CH₄ and heavy oils with the aid of so-called stoichiometric temperatures, influence of pressure on the stoichiometric points, and practical importance of the empirical determination of the properties of catalysts with the aid of adsorption measurements.

3547. VAN ISTERBEEK, A., AND VAN DINGENEX, W. [Catalytic Action of Nickel and Copper-Thorium in the Formation of Methane and Heavy Gases.] Zschr. physik. Chem., vol. 50, B, 1941, pp. 341-360; Chem. Abs., vol. 37, 1943, p. 1917. Adsorption of H₂-CO mixtures by Ni foil was determined at low pressure, less than 2 mm. Hg, and over a wide temperature range. At 167° and 329°, H₂ and CO are adsorbed in the ratio 3:1, corresponding to CH₄ formation, and, at 125° and 378°, they are adsorbed in the ratio 2:1, corresponding to higher paraffin forma-

tion. The reaction rates also show maximum at these temperatures. Cu adsorbs H₂ and to a smaller extent CO only if it contains traces of Th. At 250° and 325°, H₂ and CO are adsorbed in the ratio 3:1. Similar experiments with D are described.

3548. — [Formation of Methane in Connection With the Activated Adsorption of Hydrogen and Carbon Monoxide by Nickel and by Copper.] *Physica*, vol. 8, 1941, pp. 810-824; *Chem. Abs.*, vol. 36, 1942, p. 6062.

CH₄ forms when H₂ and CO are adsorbed on Ni. Cu acts in the same way when activated by a trace of Th. It was found that Ni shows 2 temperatures, 165° and 300°, at which the ratio of H₂:CO adsorbed is 3:1, correct ratio for CH₄ formation and, also 2 temperatures, 125° and 370°, at which the ratio is 2:1, correct ratio for benzene formation. At these exact temperatures, the reaction rate showed sharp maxima. The reaction product at 200°-300° was found to be nearly pure CH₄, but, at 165° and 400°, heavier products also occurred, which contained benzene. The same type of behavior was found for Cu; the best temperature range for CH₄ formation is 250°-525°.

VAN LOON, W. See abs. 677.

3549. VAN NOY, C. W., DUNVILLE, T. C., DRESSLER, R. G., AND CHAFFEE, C. C. Guide for Making Cost Estimates for Chemical-Type Operations. Bureau of Mines Rept. of Investigations 4534, 1949, 64 pp.

Procedure suggested in this report is intended for the use of engineers, estimators and accountants, in estimating the cost of chemical-type operations, such as the production of synthetic liquid fuels, anhydrous NH₃, and the like. It is intended to cover operating, not investment, costs.

VAN RAAY, H. See abs. 1836a.

3550. VAN VOORTHUISSEN, J. J. B. VAN E. Isomerization Equilibria of the Butanes, Pentanes, Hexanes, and Heptanes. *Rec. trav. chim.*, vol. 66, 1947, pp. 322-334 (in English); *Chem. Abs.*, vol. 42, 1948, p. 430.

Isomerization equilibria for the butanes were determined by passing C₄H₁₀ and HCl over AlCl₃ (on Norit CC) at 100°, 150°, and 200°. For the higher alkanes the determination was made in an autoclave: 100 gm. hydrocarbons, 5-10 gm. AlCl₃ (sublimed through active C at 250°), HCl, and H₂ were heated for 24 hr. as high as 80°. The products were analyzed by fractionation. Neopentane, neohexane, 3, 3-dimethylpentane, and 3-ethylpentane were not produced under these conditions, and neohexane failed to isomerize. The results for the heptanes deviated considerably from the thermodynamic predictions.

3551. VAN WINSSEN, A., AND BROWN, E. A. Superfine Asbestos. *Canadian Chem. Process Ind.*, vol. 32, 1943, pp. 129-132.

Superfine is the term applied to asbestos when opened to a degree where the individual fibers are exceedingly fine and so minute in diam. that most of them are invisible under the optical microscope. Electron microscopic study reveals the presence of fibers approximately 20 mμ diam. It is produced by wet milling in a ball or pebble mill and by subsequent spraying through a nozzle with compressed air. Its heat-resisting nature, fibrous form, and large surface area suggest the use of superfine asbestos as a catalyst or inert carrier upon which very finely divided catalyst could be deposited.

3551a. VARGA, J. [Manufacture of Motor Fuels by the Fischer-Tropsch Synthesis.] *Magyar Kém. Lapja*, vol. 5, 1930, pp. 363-368.

Summary.

VASKEVICH, D. N. See abs. 2092.

VAUGHAN, W. E. See abs. 1469.

VEDARAMAN, S. See abs. 1194.

3552. VELDE, — [Gasoline Synthesis According to Fischer-Tropsch Ruhrchemie Middle-Pressure Process.] *FIAT Reel K-25*, frames 003,957-003,978, Mar. 15, 1933; *PB* 70,216.

Survey of gasoline synthesis and calculation of the operating and installation costs for the 2-stage pressure method. (Several papers of the same content, *FIAT Reel K-25*, frames 3,974-3,978, contain the English translation of *FIAT Reel K-25*, frames 3,966-3,970). The synthesis gas (CO:H₂=1:2), is carried over Co catalysts at 175°-200° C. and raised pressure. The products are: 30% gasolinelike hydrocarbons, 30% Diesel oil, and 40% paraffinlike hydrocarbons that can be converted into gasol under weak thermal treatment with 80% yield.

3553. — [Oxidation of Paraffin With Nitrous Gases.] *FIAT Reel K-25*, frames 003,951-003,952, July 7, 1945; *PB* 70,216.

Process was carried out to produce highly molecular waxlike acids, taking care that the chain length of the paraffin hydrocarbons is spared as much as possible. After further processing, these waxlike acids can be used as substitutes for Montan waxes or I. G. Farben-industrie waxes and emulsifiers. The starting material for the production of wax acids (straight-chain fatty acids with C numbers above 18-20) was Ruhr-gasoline hard wax in refined and crude condition. It is a paraffin mixture of b. p. 400°-450° and mol. weight of about 600. At 100°-125°, paraffin is subject to the action of nitrosyl sulfuric acid and nitrous gases that are formed by NH₃ oxidation. A product that contains still unaltered starting material is formed. The pure acid can be separated by a treatment with caustic alkali solution and extraction with gasoline.

3554. VELDE, H. [Methods for Working Up the Primary Products of the Synthesis Process and Their Application to the Treatment of Petroleum.] *Oel u. Koble*, vol. 37, 1941, pp. 143-148; *British Abs.*, 1943, B, I, p. 280; *Chem. Abs.*, vol. 35, 1941, p. 8268.

Special refining method worked up by Ruhrchemie is similar to ordinary vapor-phase refining. Raw gasoline before or, preferably, after final stabilization is heated to a high temperature below the cracking temperature and led over a special catalyst, unnamed, after which the vapors are cooled and passed over the same catalyst in a 2d step at a lower temperature. Octane no. was improved by 8-24 points, the increase being independent of the original octane no. It is indicated that this effect results from an isomerization of the original material, including both branching and a change in the position of the double bond. A gasoline of 35% olefin content had an octane no. of 44, whereas, of 55% olefin content had an octane number of 41, other properties being substantially the same. The octane nos. were increased to 52 and 61, respectively, by the method discussed. The method increased the octane no. of a cracked gasoline from petroleum from 66 to 71.5. Other methods, polymerization, aromatization, and cracking are briefly discussed.

3555. — [Relation of Octane Number and Peroxide Content of Synthetic (Fischer-Tropsch) Gasoline.] *Oel u. Koble*, vol. 40, 1944, pp. 10-15; *Petrol. Refiner*, vol. 25, No. 6, 1946, pp. 137-140; *Chem. Abs.*, vol. 38, 1944, p. 5067.

Storage tests in brown and transparent bottles with and without exposure to light showed a considerable accelerating effect of light on the peroxide formation, peroxides determined by the method of Yule and Wilson, in primary synthetic gasoline (I), vapor-phase cracked synthetic gasoline (II), and a 1:1 blend of (I) and (II), (III). All the gasolines were obtained by

the Fischer-Tropsch synthesis, (abs. 1018 and 1021) or by processing material primarily made by this process. The octane numbers of samples containing an appreciable amount of peroxides decreased noticeably; the research octane number of (I) dropped from 58.0 to 37.0 when the peroxide content had reached 325 mg. O₂ per l., the octane no. of (II) fell from 68.1 to 45.0 at a peroxide content of 350 mg. O₂ per l., and (III) decreased from 65.0 to 38.5 at a peroxide number of 305 mg. O₂ per l. The same gasolines with and without the addition of alcohol, cresol, PbEt₂, or a mixture of all these additives were stored in Fe drums, and it was found that cresol inhibited the peroxide formation almost completely during a storage period of 2 yr. A definite inhibitor effect was found for alcohol with (I) and (III). PbEt₂ acted as inhibitor for gasolines stored in galvanized Fe drums but was without effect in bare Fe drums. The relation of octane no. and peroxide no. for the types of gasolines tested is shown in a diagram. Removal of peroxides by acidic FeSO₄ solution did not completely restore the original octane no.

3556. VELLINGER, E., AND THOMAS, B. [Ultraviolet Absorption Spectra of Synthetic Petroleum.] *Compt. rend.*, vol. 209, 1939, pp. 882-884; *Chem. Zentralb.*, 1940, I, p. 2455.

Spectrum of Fischer synthetic oil shows the presence of a considerable amount of aromatics. Oils obtained by the polymerization of olefins showed the same behavior. Oils were investigated that had been produced by the Fischer process and distilled in a cathodic vacuum. It was noted that as the distillation temperature increased the absorption and the density likewise increased. It appears that a part of the aromatic nuclei had become concentrated in the residue. From the position of the bands it was evident that the product consisted of naphthalene or other highly condensed nuclei.

VELTISTOVA, M. V. See abs. 728.

3557. VELITSTOVA, M. V., DOLGOV, B. N., AND KARPOV, A. Z. [Synthesis of Methanol From Water Gas Under Pressure.] *Jour. Chem. Ind. (U. S. S. R.)*, vol. 10, No. 9, 1934, pp. 24-32; *Chem. Abs.*, vol. 29, 1935, p. 1059.

Best catalyst is prepared by mixing ZnO and Cr₂O₃ and stirring with Cr₂O₃ solution to produce S₂ZnO·Cr₂O₃·Cr₂O₃·xH₂O. This is heated in a stream of H₂O and forms S₂ZnO·1.5 Cr₂O₃. At 390°-400°, 250 atm., and a gas speed of 10,000 l. per hr., this yields 1,150-1,200 gm. of MeOH per l. of catalyst per hr. Pure CO₂ and H₂ in the ratio 1:2 should be used, and no inert gas or S compound should be present, though H₂S can be reversibly desorbed from the catalyst.

VENKATESEN, C. See abs. 1189.

VERESHCHAGIN, L. F. See abs. 3559.

3558. VERESHCHAGIN, L. F., AND ZELINSKIĬ, N. D. [Chemical Reactions at High Pressures and Temperatures. I. Apparatus for the Study of Chemical Reactions at Pressures up to 5,000 Atmospheres and High Temperatures.] *Bull. acad. sci. U. R. S. S., Classe sci. chim.*, 1943, pp. 443-452 (English summary); *Chem. Abs.*, vol. 39, 1945, p. 1587.

Apparatus is described (with diagrams) for the study of reactions up to 5,000 atm. and 400°. The use of hydraulic compressors in conjunction with gas pressure as the generator of pressure permits considerable improvement in the technique of work of this type. The use of Hg as the hydraulic fluid (as previously used) is undesirable for several reasons, 1 of which is the entry of Hg into reactions under the experimental conditions.

3559. ZELINSKIĬ, N. D., AND VERESHCHAGIN, L. F. Chemical Reactions at Superhigh Pressures and High Temperatures. II. Reactions of Polymeriza-

tion of Cyclohexene and Vinylcyclohexene. *Bull. acad. sci. U. R. S. S., Classe sci. chim.*, 1943, pp. 44-51 (in English, pp. 51-52); U. O. P. Survey Foreign Petroleum Literature Transl. No. 535; *Chem. Abs.*, vol. 40, 1946, p. 5025.

Reactions of polymerization of cyclohexene, vinylcyclohexene, and unsaturated compounds of synthine under pressures up to 4,000 kg. per cm.² and at temperatures up to 300°, 350°, and 360°, respectively, were studied. The polymerization of synthine (η^2 b 1.3969; boiling up to 150°; $d^{20}_4=0.7143$; I no. 80.0) leads to the formation of oily products with a gently sloping viscosity-temperature curve. The oily product obtained in the experiment in which P=4,000 kg. per cm.², T=360°, and t=3.5 hr. was distilled under vacuum; 2 gm. were obtained, b. p. 150°-255°. The viscosity of the oil was slightly less than that of the turbine oil; η^2 b 1.4336. It congealed at 40°-45°.

VERNON, C. E. See abs. 141.

VIALLE, J. See abs. 759.

VIDT, E. J. See abs. 15a.

3560. VIGNON, L. [Action of Water Vapor on Carbon in the Presence of Lime.] *Compt. rend.*, vol. 152, 1911, pp. 871-874; *Chem. Abs.*, vol. 5, 1911, p. 2044.

If water vapor is allowed to act upon a mixture of C and CaO at 600°-800°, H₂, CH₄, and some C₂H₄ are formed besides CO and CaCO₃. The mixture of CaO and C decomposes H₂O more rapidly and at lower temperature than C alone. Much H₂O and long heating reduce the amount of CH₄ as the latter is decomposed by the H₂O to CO and H₂. The above reactions may explain the formation of marsh-gases and natural gases as well as formation of petroleum in nature.

3561. — [Formation of Hydrocarbons From Carbon Monoxide.] *Bull. soc. chim. (4)*, vol. 9, 1911, pp. 18-20; *Chem. Abs.*, vol. 5, 1911, p. 1088.

CO is converted into CH₄ by conducting CO over a mixture of CaO and Ca(OH)₂ at about 400°. The reaction takes place with the intermediate formation of Ca formate, which decomposes to give CH₄ and C₂H₄. This salt at 360°-370° gives a gas containing 20% CO₂, 27% CO, 51% H₂, and 2% hydrocarbons.

3562. — [Composition of Water Gas.] *Compt. rend.*, vol. 156, 1913, pp. 1995-1998; *Chem. Abs.*, vol. 7, 1913, p. 3405.

Water gas prepared by conducting H₂O vapor over coke, the ash of which contained 7-8% CaO, contained 3.45% CH₄, whereas water gas from C obtained from sugar, the ash of which contained 0.8% CaO, gave less than 2% CH₄, CO and CO₂ having been removed. Mixing coke with CaO and passing H₂O vapor over the mixture, there were obtained, with 1% CaO at 1,000°, 12% CH₄; with 13% CaO at 1,000°, 19% CH₄; with 33% CaO, 23% CH₄, CO and CO₂ removed. Following reactions take place: (1) 4CO+2H₂O=3CO₂+CH₄; (2) 2CO+2H₂=CO₂+CH₄; (3) CO+4H₂=CH₄+2H₂O.

3563. — [Formation of Methane by Catalysis From Carbon Monoxide and Water Vapor.] *Compt. rend.*, vol. 157, 1913, pp. 131-134; *Chem. Abs.*, vol. 7, 1913, p. 3602.

Substances studied as catalyzers were Fe, Ni, Cu, and the oxides of Si, Al, and Mg. The catalyzers were placed in a glazed porcelain tube and heated at different temperatures in the electric furnace, the temperature being taken from the midst of the catalyzer by a Le Chatelier couple. The temperatures at which a maximum yield of CH₄ was obtained and the % present in the resulting gas after deducting CO₂ and CO are as follows: Al₂O₃, 950°, 39.1%; MgO, 900°, 38.7%; SiO₂, 750°, 43.5%; Fe, 950°, 35.5%; Ni, 400°, 89.3%; Cu, 700°, 74.1%. With Fe, Al₂O₃, and SiO₂, carbides are evidently an intermediate product and these carbides, as soon as formed, are acted upon by H₂O vapor with

- the formation of CH_4 : for example, $12\text{CO} + 2\text{Al}_2\text{O}_3 = \text{C}_2\text{Al}_4 + 9\text{CO}_2$; $\text{C}_2\text{Al}_4 + 6\text{H}_2\text{O} = 3\text{CH}_4 + 2\text{Al}_2\text{O}_3$. Another explanation for the formation of CH_4 is that under the influence of catalysts the following reactions take place: $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$; $3\text{H}_2 + \text{CO} = \text{CH}_4 + \text{H}_2\text{O}$; $4\text{H}_2 + \text{CO} = \text{CH}_4 + 2\text{H}_2\text{O}$.
3564. ———. [Water Gas.] *Ann. chim.*, vol. 15, 1921, pp. 42-60; *Chem. Abs.*, vol. 15, 1921, p. 2712.
- It has been found that moist CO and H_2 react to form small amounts of CH_4 , the proportions at 400° , after absorption of CO and CO_2 , being H: CH_4 99.8% and CH_4 : 0.2% and at $1,800^\circ$, 98.65% and 1.35%. The catalytic effect of various mineral constituents of the ash of gas coke on the formation of CH_4 is discussed.
- VILESOVA, G. F. See abs. 569.
3565. VINCENT, J. W. Aspects of the Synthetic Fatty Acid and Synthetic Fat Industries in Germany. *Chem. Trade Jour.*, vol. 119, 1946, pp. 635-637; *Petrol. Times*, vol. 51, 1947, p. 283; *BIOS Final Rept.* 805, 1946, 99 pp.; PB 49,196.
- During the war Germany operated 3 synthetic fatty acid plants: Witten (Ruhr), now in the British zone with intake capacity 40,000 tons per yr.; Oppau (Ludwigshafen), now in the French zone, 20,000 tons; and at Heydebrech, now in the Russian zone, 20,000 tons. A 4th plant, 12,000 tons, also was completed toward the end of the war at Leuna, now in Russian zone, but was not operated during the war. There was a synthetic fat plant at Witten. The raw material was Fischer-Tropsch gatsch b. 320° - 450° C. or paraffin from hydrogenation of brown coal. A report of Mersol and Mersolate manufacture is given. I. G. Farbenindustrie's Mersol plants were located at Leuna (Merseburg), 50,000 tons, and Wolfen, 35,000 tons, both now in the Russian zone. The Witten plant owned by the Deutsche Fettsäurewerke, and the Oppau plant owned by I. G. Farbenindustrie have recently been operated. Witten, 20,000 tons, Oppau, 10,000 tons, with full capacity promised in 6 months. The Oppau plant is being repaired in anticipation of an offer from the Russian zone of 500-1,000 tons per month of brown-coal hydrogenation wax from Saxony. The Trade and Industries Division of the British Military Government is considering repair of Krupp and Victor Fischer-Tropsch plants to provide gatsch for the Witten plant. It is proposed to use the Ruhrchemie Fe catalyst and to examine the possibility of cracking the high-melting-point gatsch. As a result of laboratory work, Witten has reported favorably upon use of a rather oily slack wax from spindle oil refining at the Deurg-Neurag refinery at Misburg (near Hanover) and unfavorably upon a similar sample from neutral oil refining. Oppau has reported favorable results with these 2 slack waxes. Based on German data, costs for operating similar plants in the United Kingdom have been worked out. The figures are £96 10 s. 2 d. (Oppau) and £91 0 s. 4 d. (Witten) per metric ton of mixed fatty acids, which compare unfavorably with current market values. The cost of imported wax accounts for nearly $\frac{2}{3}$ of this cost, however. The synthetic-fat plant is in operation, 350 tons per mo. Estimated costs of production in England was £205 4s. 1 d. per ton. The Oxo plant at Oberhausen has been 90% repaired. The usual feed stock for the mersol plants was mepasin or hydrogenated Fischer-Tropsch kogasin with b. p. 230° - 320° C., though Witten also operated at times on heavy Fischer-Tropsch fractions. The hostapon process at Leuna is in direct production of alkyl sulfonic acids by sulf-oxidation of mepasin using SO_2 and O_2 , the reaction being promoted either by ultraviolet light or by the use of acetic anhydride as catalyst. The I. G. Farbenindustrie chemists favored acetic anhydride.
- VITRIKH, M. V. See abs. 2658.
3566. VLUGTER, J. C. Manufacture of Mersolate in Germany. *BIOS Final Rept.* 1130, February 1947, 29 pp.; PB 75,845.
- Mersolates are sodium alkyl sulfonates and are prepared by reacting a paraffinic-base material (a saturated gas-oil fraction from Fischer-Tropsch products) under influence of light with SO_2 and Cl and saponifying the resulting intermediate product, Mersol, by means of NaOH. A description of the process and the reaction conditions of the sulfochlorination and saponification are given. Several plant installations are described and translation is made of a report by Dr. Hagge and Dr. Korn on the preparation and saponification of Mersol with recommendations for the design of a Mersolate plant with a capacity of 15,000 tons of active material per yr.
3567. ———. [Synthetic Detergents, Production of Mersolates in Germany.] *Chem. Weekblad.*, vol. 45, 1949, pp. 198-199.
- Digest of a paper presented to the Netherlands Chemical Society, July 1948. 3 sources of detergents by way of the Fischer-Tropsch process are mentioned. The Fischer-Tropsch paraffins b. 320° - 450° were utilized to produce 40,000 tons of synthetic soap per yr. The gasol fraction b. 240° - 320° from the Mersol process produced a capacity of 80,000 ton of mersolate per yr. The Oxo process by preparation of primary alkylsulfates from C_2 - C_4 olefins gave a possible production of 10,000 tons. The mersol process is considered the most important source of detergents and, therefore, is described at greater length.
3568. VOGEL, H. [Synthesis and Polymerization of Formaldehyde.] *Helv. Chim. Acta.*, vol. 11, 1928, pp. 370-371; *British Chem. Abs.*, 1928, A, p. 508; *Chem. Abs.*, vol. 22, 1928, p. 1756.
- When a mixture of equal volumes of CO and H_2 was passed at 150° - 180° over a mixture of pumice and Zn dust with 2% of MgO and 1% of PbO, formaldehyde was formed together with caramellike polymerization products.
3569. VOGEL, J. C. Oil From Coal in South Africa. *South African Min. and Eng. Jour.*, vol. 51, 1940, pp. 107-109; *Coke Smokeless-Fuel Age*, vol. 3, 1940, p. 48.
- Describes the essential features of the 3 types of processes—carbonization, hydrogenation, and synthesis—with special reference to South African conditions. There is no low-temperature-carbonization plant and little promise of an adequate market for the semicoke. Coal carbonization cannot be regarded as a major source of indigenous oil fuel. The establishment of a coal-hydrogenation industry in South Africa is mainly a question of economics. As regards synthesis, bituminous coal would have to be the fuel used. Separate carbonization of the coal and gasification of the coke probably would be too expensive and some form of direct gasification would have to be used. Coals of the Vereeniging and Breyten areas, seams 1 and 4 of the Witbank area, and the semianthracites of Natal all appear to meet the requirements. From the standpoint of raw material, the synthetic process has much wider scope than the others in the Union, and the investment required may be much less than for a hydrogenation plant.
3570. VOGEL, R., AND DÖRING, W. [Iron-Cementite-Manganese Carbide-Manganese.] *Arch. Eisenhüttenw.*, vol. 9, 1935, pp. 247-252; *Chem. Abs.*, vol. 30, 1936, p. 710.
- Former investigations of this system and parts of it were enlarged and completed by establishing the constitutional diagrams on the basis of heats of reaction and structure. Mn and Mn_3C do not form, as indicated previously, an uninterrupted series of solid solutions with a maximum temperature; a transition

- equilibrium occurs at solidification between 1.5 and 2% C, which leads toward higher C contents, to a minimum temperature. A new transformation of Mn carbide was observed at $1,050^\circ$. Four kinds of crystals were found in the system Fe-Fe₃C-Mn₃C-Mn: Ternary solid solutions of $\alpha(\delta)$ -Fe with C and Mn, which are restricted to a small range in the Fe-corner; ternary solid solutions of γ -Fe with C and Mn with a very extended range; ternary solid solutions of γ -Mn with α and Fe (area $\alpha\beta\gamma\delta$); and solutions Fe₃C and Mn₃C (area $\delta\beta\gamma\delta$). The cementite does not form solid solutions with the excess Fe but the Mn₃C does with excess Mn. The conditions are explained in detail by the diagram. A table shows the location of the characteristic points α , β , γ , δ , and ϵ for the equilibria of the Fe-Mn-C alloys in solid state. Various structures illustrated in photomicrographs.
3571. VOIRET, E. G. [Motor-Fuel Problem in France.] *Chim. et ind.*, vol. 56, No. 5, 1946, pp. 423-428.
- Discusses main means by which the motor-fuel requirements of France can be met from internal resources. By utilization of gas producers, distillation or gasification of lignites, coal and bituminous shales, and manufacture of certain synthetic fuels, at least the vital minimum of motor fuels can be produced from native resources on an economic basis, and probably a large measure of independence of foreign supplies be secured. It is considered that the synthesis of liquid fuels by the Bergius, Pott-Broche, Fischer, and Mines of Béthune methods is not economically attractive under normal circumstances, but a partial exception is made in favor of the synthesis of MeOH from Faveau lignites. The requisite mixture of CO and H_2 also may be obtained by processing coke or by converting CH_4 .
- VOLKOVA, A. A. See abs. 849.
3572. VOLMER, W. [Fischer-Tropsch Hydrocarbon Synthesis.] *Ztschr. Elektrochem.*, vol. 54, 1950, pp. 252-254; *Chem. Abs.*, vol. 45, 1951, p. 1749.
- Attempt to obtain information on the mechanism of the Fischer-Tropsch synthesis by studying the statistical distribution of hydrocarbons in the product.
- VOL'NOV, Y. N. See abs. 1795, 1796.
3573. VON FREDERSDORFF, C. Continuous Gasification of Powdered-Coal Suspensions by Air-Oxygen and Air-Oxygen-Steam Mixture. *Proc. Am. Gas Assoc.*, vol. 31, 1949, pp. 705-724; *Chem. Abs.*, vol. 44, 1950, p. S623.
- Describes operation and results of a laboratory-scale coal-gasification unit. Results define the variables affecting the process and indicate the magnitudes of the effects. It is indicated that (1) a slugging operation can be applied successfully to suspension gasification at atmospheric pressure, (2) low gas-residence time is advantageous in increasing the make-gas calorific value, (3) tangential firing can remove more than 50% of the ash in the form of slag, and (4) the use of a combustion tube in the center of the gasifier does not yield any thermal advantage over operation without a tube. Although a satisfactory gasification was accomplished from the standpoint of gas calorific value, it will be necessary to use steam superheated to at least $2,000^\circ$ F. to decrease the make-gas CO_2 content, decrease the O_2 required for gasification, increase the CO conversion, and shift the point of maximum thermal efficiency to closer correspondence with the point of maximum calorific value. Anticipated benefits of the process for the industry include the production of a low-cost base or carrier gas for blending purposes, a gas of intermediate calorific value by oil carburetion of the hot exhaust of the gasification furnace, and a gas of adjusted H₂:CO ratio suitable for synthesis purposes.
- 3573a. VON FREDERSDORFF, C. G., AND PYRCIOCH, E. J. Pressure-Gas Oxygen Coal Gasifier. *Am. Gas Assoc. Monthly*, vol. 34, September 1952, pp. 38-35, 46-47.
- Series of some 20 successful runs were made to explore the effects of O_2 enrichment, O_2 : coal ratio and gasification pressure on the gas heating value and conversion efficiency of the continuous, pulverization-pressure gasification process developed at the Institute Gas Technology. Using a high-volatile C Illinois No. 6-seam bituminous coal containing approximately 8% ash, a range of pressure from 2-5 atm., O_2 : coal ratios from 0.7-1.0 lb. per lb. and O_2 concentrations 21-70%, were explored. The gasification results are summarized. Gases produced varied from a 150 B. t. u. producer gas using 30% O_2 concentration to a 240 B. t. u. synthesis gas with 70% O_2 concentration. The gas heating value generally increased by 5 B. t. u. per ft.³ with each atm. increase in gasification pressure. Gas heating value reached a maximum in the range 0.7-0.85 lb. per lb. coal. With a constant steam: coal ratio of 1.0 lb. per lb., the ratio H₂:CO varied 0.95-1.4 depending on the O_2 : coal and O_2 concentration used. Maximum values of steam decomposition of $>50\%$ occurred when the O_2 : coal ratio was approximately 0.9 lb. per lb. The % C gasified increased rapidly with O_2 : coal ratio and attained values of over 90% at 0.85 lb. O_2 per lb. coal. C gasification increased generally by 4% for each atm. increase in gasification pressure. The cold gas efficiency increased with both O_2 : coal ratio and gasification pressure and attained maximum values of nearly 75% based on heating value of the coal. The O_2 , coal and steam requirements per 1,000 ft.³ synthesis components (CO+H₂) were greatly influenced by both the O_2 : coal ratio and gasification pressure. Minimum requirements were as low as 33 lb. steam, 33% coal and 300 ft.³ total O_2 . The coal ash removed in the process as dust and slag was as high as 100% of the total ash fed in the coal. On the basis of \$0.06 per 1,000 ft.³ compressed air, \$5.00 per ton O_2 , \$4.00 per ton slack coal and allowing \$0.30 per 1,000 lb. process self-generated and self-superheated steam, the synthesis gas raw material cost varies 14.5-16.2 cents per 1,000 ft.³ of CO+H₂ depending on the amount of O_2 enrichment.
- VON PHILIPPOVICH, A. See abs. 998, 3462, 3463, 3464.
- VON RENNENKAMPFF, J. See abs. 1180, 1181.
3574. VON SELASINSKY, A. [Soap From Coal.] *Rundschau deut. Tech.*, vol. 18, No. 1, 1938, p. 9; *Chem. Abs.*, vol. 32, 1938, p. 3170.
- Historical review, especially describing the Imhausen-Troschke process and its importance for Germany's economic situation.
- VON SETHI, R. See abs. 1622, 1623.
3575. VON STACKELBERG, M. [Investigations on Carbides. I. Crystal Structure of Carbides MeC.] *Ztschr. physik. Chem.*, vol. 9, 1930, B, pp. 437-475; *Chem. Abs.*, vol. 25, 1931, p. 11.
- X-ray investigation by the powder method of a series of carbides of formula MeC, shows that they have a face-centered tetragonal lattice with 4 mol. in the unit cell and lattice constants as follows, recording a , c , and the density in order: CaC₂, 5.48, 6.87, 2.21; SrC₂, 5.81, 6.68, 3.29; BaC₂, 6.22, 7.06, 3.90; LaC₂, 5.54, 6.55, 5.35; CeC₂, 5.48, 6.48, 5.56; PrC₂, 5.44, 6.38, 5.75; NdC₂, 5.41, 6.23, 6.08; ThC₂, 5.55, 5.28, 9.3; NaHC, 5.40, 8.17, 1.33; KHC, 6.05, 8.42, 1.37. The C-C distance in the C₂ group is 1.4 Å. U, agreeing with band spectra data. With the help of the polarizing microscope the tetragonal symmetry was confirmed for CaC₂, SrC₂, and BaC₂. An electron configuration similar to that of the N₂ molecule is postulated for the C₂ and HC₂ groups. The possible space-group classifications are discussed. These

carbides appear to show a new lattice type somewhat similar to that of pyrite.

3576. —. [Crystal Structures of Several Carbides and Borides.] *Ztschr. Elektrochem.*, vol. 37, 1931, pp. 542-545; *Chem. Abs.*, vol. 25, 1931, p. 5812.

In order to form a carbide of the Ca₂C type, hydrolyzing to C₂H₂ with H₂O, a minimum metal-ion size is necessary. The metallic properties of most carbides of this formula are due to the presence of 2 extra valence electrons. Ca, Sr, Ba, La, Ce, and Th form borides of formula MeB₃ with CsCl-type cubic lattice.

3577. —. [Structural Principle of Carbides, Silicides, Nitrides, and Phosphides of Electropositive Metals.] *Ztschr. physik. Chem.*, vol. B 27, 1934, pp. 53-57; *Chem. Abs.*, vol. 29, 1935, p. 657.

Compounds of Be, Al, Mg, Ca, Si, Ti, and Zr with C, Si, N, and P are considered as forming ionic-crystal lattices. The anions assemble in a lattice of the closest spherical packing. The cations are embedded in the tetrahedral or octahedral gaps in the lattice.

3578. VON WARTENBERG, A., MUGHELINSKI, A., AND RIEDLER, G. [Investigation of Formaldehyde.] *Ztschr. angew. Chem.*, vol. 37, 1924, pp. 457-459; *Chem. Abs.*, vol. 19, 1925, p. 769.

Attempts were made to synthesize CH₂O by subjecting a mixture of CO+H₂ to the silent electric discharge in an ozonizer. The voltage, pressure, temperature, and time of contact were varied over wide limits, but only traces of CH₂O were ever obtained; indeed, a mixture of CH₂O+H₂ was decomposed by the electric discharge. From the Nernst heat theorem, it appears that the equilibrium is favorable for the formation of CH₂O from COCl₂+2 H₂. The best yield obtained, at 300° with Ni catalyst, was 3.6%. The chief reaction was decomposition of the COCl₂ to CO and HCl. The oxidation of CH₂ with O₂ to give CH₂O was tried with a large number of catalysts, of which PbCrO₃ proved to be the best; but the highest yield obtained, at 650°, was only 2% based on CH₂.

3579. VON WARTENBERG, H., AND LERNER-STEINBERG, B. [Heat of Formation of Formaldehyde.] *Angew. Chem.*, vol. 38, 1925, pp. 591-592; *Chem. Abs.*, vol. 19, 1925, p. 3202.

For the heat of formation from CO+H₂+1.4 cal. is obtained.

3580. VON WAUGENHEIM, F. [Preparation of Carbon From Carbon Monoxide.] *Brennstoff-Chem.*, vol. 8, 1927, pp. 385-388; *Ges. Abhandl. Kenntnis Kohle*, vol. 8, 1929, pp. 227-233; *Chem. Abs.*, vol. 22, 1928, p. 2641.

Attempt was made to prepare pure C by passing CO over a pure Fe₂O₃ catalyst at temperatures under 650°. The reduced Fe was removed from the prepared C by vaporization in a current of Cl₂. The recovered C was not entirely Fe-free, but it was nonmagnetic. It was a good conductor of electricity.

3581. VON WAUGENHEIM, F., AND WINKELMANN, —. [Production of Pure Carbon at Low Temperature.] *Thesis*, Cologne, 1924; *Ges. Abhandl. Kenntnis Kohle*, vol. 8, 1929, p. 235.

Formation of C on a reduced Fe catalyst proceeds only to a definite point, beyond which the activity of the catalyst virtually ceases. The limit was established by a reduction in concentration of the Fe to about 1%. The breakdown in the catalyst activity at a definite reduction of the Fe was believed to be due to the

3588. WACHS, W., AND REITSTOETTER, J. [Synthetic Fats in Germany.] *Angew. Chem.*, vol. 20, B, 1948, pp. 61-68; *British Abs.*, 1948, B, II, p. 547; *Chem. Abs.*, vol. 42, 1948, p. 7067.

formation of a solid solution of a higher carbide and C from which the catalytically active Fe₂C could not be regenerated.

3582. VON WEBER, U. [Determination of Branched Isomers in Mixtures of Paraffin Hydrocarbons.] *Angew. Chem.*, vol. 52, 1939, pp. 607-610; *Chem. Abs.*, vol. 34, 1940, p. 365.

Information on the isomeric composition of Fischer-Tropsch hydrocarbons. The method is explained in detail. By determining boiling points and molecular weights of fractions, it is estimated that the mole fractions of branched hydrocarbons are 0.15, 0.27, and 0.40 for the C₆, C₈, and C₁₀ ranges, respectively.

3583. VON WETTERBERG, E. F., JR., AND DODGE, B. F. Methanol Equilibrium. *Ind. Eng. Chem.*, vol. 22, 1930, pp. 1040-1046; *Chem. Abs.*, vol. 24, 1930, p. 5718.

Equilibrium in the reaction CO+2 H₂=CH₃OH was determined at 170 atm. and temperatures ranging 258°-329°. Zn-Cr and Zn-Cu catalysts were used. The new data differ considerably from results by theoretical methods, and various sources of error in the latter are pointed out. The results of various investigators are summarized in tabular form.

3584. Voos, W. [Manufacture of Catalysts for the Synthesis.] *FIAT Reel K 21*, no date, frames 893-898; *PB 70,212*; *TOM Reel 2SS*.

Invention is discussed for making catalysts of the metal group Co-Ni-Fe possessing a surface activity as yet unattained elsewhere. Because of the very fine distribution, they provide immeasurable possibilities for being used in the synthesis of fuels or catalysis in related fields, as well as in the hydrogenation of vegetable and animal oils.

3585. VORRACH, —. [Experiments With Silica Gel as a Carrier for Cobalt Catalysts in the Synthesis of Gasoline From Carbon Monoxide and Hydrogen.] *FIAT Reel R-20*, June 3, 1940, frames 7537-7540; *PB 73,564*.

Report from the I. G. Ammonia Laboratory, Oppau, deals with experiments to determine the influence of the size of pores in silica gel used as a carrier substance in the synthesis of gasoline. It is obvious that the size of pores is important. Small-size silica gel ignited at 1,000° proved to be an easily reproducible carrier substance, which can fully replace diatomaceous earth in synthesizing gasoline from CO and H₂.

3586. VORBEMA, G. [Problems of the Production of Liquid Fuels From Coal.] *Seifensieder-Ztg.*, vol. 72, 1946, pp. 146-149, 166-168; *Chem. Abs.*, vol. 43, 1949, p. 6390.

Most important processes are discussed, including high-pressure hydrogenation, low-pressure synthesis, the Fischer-Tropsch process, and the extraction process of Pott and Broche.

3587. Voss, —. [New Syntheses in the Solvent Industry.] *Kunststoffe*, vol. 17, 1927, pp. 79-80, 132-134, 205-207; *Chem. Abs.*, vol. 21, 1927, p. 3993.

Recent patents are reviewed on processes dealing with the generation of MeOH from water gas, direct oxidation of CH₄ to MeOH, manufacture of MeCl and MeBr from CH₄, and the oxidation of these to MeOH, and the manufacture of MeOH from CO.

Voss, D. J. *See abs.* 3153a.

VVEDENSKII, A. A. *See abs.* 3030.

Fatty acids are produced by oxidation of paraffins from brown coal and from synthetic wax with air at 100° and 1 atm. in presence of a catalyst, KMnO₄, which accelerates the formation of peroxides on which

the chain reaction depends. The treatment is stopped when about 40% of the paraffins have been attacked in order to reduce secondary oxidations. The purification by vacuum fractionation at 2-5 mm. Hg and esterification with glycerol of the C₁₂-C₁₈ fraction to produce edible fat are outlined. Acids from Fischer-Tropsch wax include branched-chain members, which must be removed for physiological reasons. Fatty acids and sulfonate detergents and wetting agents from the lower fractions obtained by this process are used to replace soaps from natural fats for washing and industrial purposes.

3589. WAGMAN, D. D., KILPATRICK, J. E., TAYLOR, W. J., PITZER, K. S., AND ROSSINI, F. D. Heats, Free Energies, and Equilibrium Constants of Some Reactions Involving O₂, H₂O, C, CO, CO₂, H₂, CH₄. *Jour. Research, Nat. Bureau of Standards*, vol. 34, 1945, pp. 143-161, Research Paper 1634; *Chem. Abs.*, vol. 39, 1945, p. 2440.

Values are given for: The heat-content function, (H°-H°₀)/T, the free-energy function, (F°-H°₀)/T, the entropy, S°, the heat content, H°-H°₀, and the heat capacity, C_p°, for: O₂(g), H₂(g), N₂(g), CO(g) all to 5,000° K.; H₂O(g) to 3,000° K.; CO₂(g) to 3,500° K.; CH₄(g) to 1,500° K.; C(solid, graphite) to 1,500° K.; C(solid, diamond) to 1,200° K. Also given are: The standard entropy, S°, for H₂O(lq) at 25°; the heat of formation, the free energy of formation, and the equilibrium constant of formation from the elements, for H₂O(lq) at 25° and for H₂O(g), CO(g), CO₂(g), and CH₄(g) at 1,500° K.; the increment in heat content and free energy for the transition of graphite into diamond at 1,200° K. and 20,000 atm. From the foregoing, values were calculated for ΔH°, ΔF°, and the equilibrium constant to 1,500°K. for the following reactions, most of which are important in connection with the production of liquid hydrocarbon fuels from natural gas or coal and H₂: C(solid, graphite)+CO₂(g)=2 CO(g); C(solid, graphite)+H₂O(g)=CO(g)+H₂(g); CO(g)+½O₂(g)=CO₂(g); CO(g)+H₂O(g)=CO₂(g)+H₂(g); CH₄(g)+½ O₂(g)=CO(g)+2 H₂(g); CH₄(g)+CO₂(g)=2 CO(g)+2 H₂(g); CH₄(g)+H₂O(g)=CO(g)+3 H₂(g); CH₄(g)+2 H₂O(g)=CO₂(g)+4 H₂(g).

WAGNER, E. O. *See abs.* 2576, 2577.

3590. WAGNER, K. H. *Synthetic Fats*. *Bib. Sci. Ind. Repts.*, vol. 7, No. 6, Nov. 7, 1947, pp. 535-536; *PB 85,791*, 1947, 157 pp.

This comprehensive report deals essentially with 4 viewpoints: Production of synthetic fats to be used as food; changes of fats during storage; physiology of the fat metabolism; and synthetic fat in animal experimentation and human pathology. The starting materials for the production of synthetic fats are the fatty acids, which are obtained from the paraffins of the Fischer-Tropsch process by catalytic oxidation with atm. O₂, subsequently esterified with glycerol. Data necessary for cost calculations are given.

WAINWRIGHT, H. W. *See abs.* 144a, 3023, 3024, 3025.

3591. WAINWRIGHT, H. W., AND LAMBERT, G. I. Colorimetric Method for the Determination of Thiophene in Synthetic Gas. *Bureau of Mines Rept. of Investigations* 4753, 1950, 11 pp.

Study of the isatin method is reported. Variables investigated included aging of reagent, temperature, influence of oxidizing agents, and interference due to the presence of CS₂, C₂H₅SH, and olefins. A procedure was developed for carrying out the analysis, and its applicability to synthesis gas containing low concentrations (less than 2%) of olefins was proved valid. It is claimed that as little as 0.0001 grain of thiophene S per 5.5 ml. of test reagent can be detected by de-

termining color intensity with a Beckman spectrophotometer at a wavelength of 580 mμ, using a 10-mm. light path.

WALENDA, H. *See abs.* 2687.

WALKER, J. *See abs.* 9, 10.

3592. WALKER, J. C., AND MALAKOFF, H. L. Basic Oxygenated Chemicals From C₂, C₃, and C₄ Paraffins and Olefins. *Petrol. Refiner*, vol. 25, 1946, pp. 607-612; *Oil Gas Jour.*, vol. 45, No. 33, 1946, pp. 59, 60, 62, 65; *Chem. Abs.*, vol. 41, 1947, p. 1598.

Four methods for producing oxygenated hydrocarbons are discussed briefly: (1) Direct oxidation; (2) dehydrogenation followed by oxidation and hydration; (3) oxidation to CO and H₂, followed by hydrogenation of the CO; (4) chlorination followed by hydrolysis. With the aliphatic gases as raw materials in the direct-oxidation process, a typical oxygenated crude liquid will contain about 35% MeOH, 20% HCHO, and 5% AcH as principal products. Partial oxidation of natural gas to CO and H₂ for production of MeOH, which by further oxidation yields HCHO, has been the impetus to the development of the bakelite-type plastics industry. The production of EtOH from C₂H₄, illustrates commercial production by hydration, which is displacing older established methods. C₂H₄, which is expected to be available at \$0.02 per lb., will reduce the cost of synthetic EtOH to \$0.10 per gal. Future oxidation processes now in the pilot-plant stage include the Fischer-Tropsch, nitration, thermal cracking plus hydration, and electric discharge plus hydration.

3593. WALKER, S. W. *Manufacture of Synthetic Gasoline*. *Oil Gas Jour.*, vol. 46, No. 8, 1947, p. 126; *Nat. Petrol. News*, vol. 39, No. 26, 1947, p. 44.

Paper presented at Midwest Regional Meeting, American Chemical Society, Kansas City. Improvements in the Fischer-Tropsch process and use of low-cost natural gas and O₂ have resulted in an economic process for the synthesis of gasoline and byproduct chemicals. The substitution of a fluidized Fe catalyst for the German fixed Co catalyst has resulted in better heat control, higher-quality gasoline, fewer undesirable products, and lower investment costs. Production of the synthesis gas by partial combustion of natural gas is an innovation which depends on cheap O₂ from the modified Linde-Frankl process and is a more efficient process than CH₄ reforming or the steam and coke method. It is estimated that 360,000 lb. per day of crude, H₂O-soluble chemicals will be produced in each of the 2 plants now under construction. These consist primarily of alcohols, aldehydes, acids, and ketones and are found mostly in the H₂O stream from the oil-recovery section from which they may be separated into the various components. The oil stream also contains oxygenated compounds of the same general type having 4 or more C atoms; these are less important industrially at the present time, since their availability in quantity is limited. However, the development of satisfactory recovery and separation processes for these compounds will encourage investigation of their commercial uses. The chief end product of the process is, of course, gasoline, which can be produced in the form of an approximate 80-octane no. fuel in competition with natural petroleum products of equivalent quality, taking into account operating and amortization costs with natural gas at prevailing prices. It is indicated that the investment for a synthetic oil plant is approximately \$3,000-\$3,500 per daily bbl. of hydrocarbon products, or less than half the corresponding figure for the German plants.

— *See abs.* 2069.

WALLIS, A. E. *See abs.* 2308.

WALTER, K. *See abs.* 1088, 1089.

3594. WALTHER, C. [Technique of Oil Synthesis.] Arch. Warmewirt., vol. 15, 1934, pp. 23-24.

Discusses liquefaction of coal and other synthetic processes for production of hydrocarbons, synthetic lubricating oils, and liquid fuels from gases.

WANGENHEIM, F. See abs. 1027, 1028.

3595. WARD, C. C., SCHWARTZ, F. G., AND ADAMS, N. G. Composition of Fischer-Tropsch (Cobalt Catalyst) Diesel Fuel. Ind. Eng. Chem., vol. 43, No. 5, 1951, pp. 1117-1119.

Sample of diesel fuel prepared by the German modification of the Fischer-Tropsch process, using a Co catalyst, was fractionated and analyzed by use of refractometric and spectrographic methods. The sample contained about 2% of oxygenated material, which was removed by percolating the sample through silica gel. 80 gal. of the percolate was fractionated at reduced pressure, and 177 0.5% fractions were collected. The density, refractive-indexes, Br number, and cetane number were determined on each fraction and the infrared spectra on selected fractions. The approximate composition of the fuel was as follows, in %: Oxygenated compounds, 2; α -type olefins, 1.5; internal-type olefins, 5.5; paraffins, 88. Engine tests on several of the fractions indicated ratings higher than cetane, showing the need for a standardized method of rating Diesel fuel components that have a cetane number of more than 100.

3596. WARD, S. G. Coal—Its Constitution and Utilization as a Chemical Raw Material. Canadian Chem. Process Ind., vol. 31, 1947, pp. 626-636.

First Westman Memorial Lecture. Includes discussions of the formation and composition of coals, thermal decomposition, action of solvents, action of chemical reagents, methods of utilizing and processing coal, such as complete gasification, coal hydrogenation, Pott-Broche process, Fischer-Tropsch synthesis process, and direct utilization of coal gas as a chemical raw material. Bibliography with 68 refs.

3597. WARDEN, C. P. Production of Oils From Coal. Jour. Chem. Met. Min. Soc. South Africa, vol. 38, 1937, pp. 1-21; vol. 38, 1938, pp. 342-347; Chem. Abs., vol. 31, 1937, p. 8886; vol. 32, 1938, p. 4752.

Conversion of coal into oils requires 2 operations: (a) Reduction in molecule size from more than 2,000 to 100-400, and (b) the H:C ratio must be increased—for coal from 0.65 to 1.90 and for tar from low-temperature carbonization from 1.25 to 1.90. To do this, 3 types of operations may be used: (1) Carbonization, (2) hydrogenation; or (3) catalytic synthesis. Each is discussed. Flow sheets for 4 types of plants to produce oil from South African coal are presented and discussed.

3598. WARDENBERG, F. A. High-Pressure Synthesis as Applied to the Manufacture of Things in Everyday Use. Jour. Franklin Inst., vol. 221, 1936, pp. 449-464; Chem. Abs., vol. 30, 1936, p. 3930.

Synthesis of NH₃ and MeOH is described with historical and economic comment.

3599. WAERNER, B. R., DERRIG, M. J., AND MONTGOMERY, C. W. Catalytic Synthesis of Hydrocarbons and Oxygenated Compounds From Ketenes and Its Relation to the Fischer-Tropsch Synthesis. Jour. Am. Chem. Soc., vol. 68, 1946, pp. 1615-1617; Chem. Abs., vol. 40, 1946, p. 7149.

The fact that CH₂ and CO can combine to form ketene (CH₂CO) indicates the possibility that ketene may form and may be intermediate in the Fischer-Tropsch synthesis. Experiments determined that CH₂CO in the presence of H₂ reacts on a Co-ThO₂-kieselguhr catalyst at 200° to yield hydrocarbons and oxygenated compounds, which are similar to the prod-

ucts of the Fischer-Tropsch synthesis. A reasonable assumption to explain the experimental results involves preliminary catalytic decomposition of CH₂CO→CH₂+CO followed by polymerization of CH₂, or by reactions involving higher ketenes and formation of oxygenated compounds. A reaction mechanism for the Fischer-Tropsch synthesis might be postulated as follows: (a) CH₂CO→CH₂+CO; (b) CH₂+CH₂CO→CH₂CH₂CO; (c) CH₂CH₂CO→C=O→CH₂CH₂CO; (d) CH₂+CH₂CH₂CO→C=O→CH₂CH₂CH₂CO.

3600. WARREN, T. E. Inspection of Hydrogenation and Fischer-Tropsch Plants in Western Germany During September 1945. BIOS Final Rept. 82, 1945, 28 pp.; PB 7,917 and PB 27,316; TOM Reel 199.

General survey of plants and processes largely covered in other reports already abstracted.

3601. ———. Factors Influencing Establishment of a Synthetic Liquid-Fuel Industry in Western Canada. Canadian Chem. Process Ind., vol. 31, 1947, p. 644.

Paper presented at the 3d annual meeting of the Chemical Institute of Canada. The situation regarding supply and requirements of petroleum in western Canada is considered in conjunction with the raw materials and processing methods that might conceivably be used for the production of petroleum substitutes. 2 basic methods, direct hydrogenation and hydrocarbon synthesis, are considered in their application to 3 types of raw material, natural gas, asphaltic oil, including bitumen, and coal. There is uncertainty at present regarding several factors that should be taken into consideration in planning the establishment of a synthetic liquid-fuel industry.

3602. ———. Petroleum Substitutes in Canada. Chem. and Eng. News, vol. 25, 1947, p. 1857.

Paper presented at the meeting of the Chemical Institute of Canada. Discusses the processing methods that might be used for the production of petroleum substitutes. The natural-gas reserve in Alberta is estimated at 1-2.5 trillion cu. ft., enough to last a minimum of 22.3 yr. at the present rate of consumption or 16.1 yr. with a synthesis plant of 5,000 bbl. per day capacity. There also is enough coal in western Canada to supply a Fischer-Tropsch plant of 30,000 bbl. per day capacity for 2,000 yr. Coal hydrogenation is considered too expensive a method to be used in Canada unless the equipment could be simplified by the use of higher pressures. The deposits of tar sands in western Canada containing 350,000,000 bbl. of bitumens would supply a 30,000 bbl. per day hydrogenation plant for 25-30 yr.

3603. ———. Factors Influencing the Establishment of a Synthetic Liquid-Fuel Industry in West Canada. Canadian Chem. Process Ind., vol. 32, 1948, pp. 318-321; British Abs., 1950, B, I, p. 173.

Methods and materials that might be used by a synthetic-oil industry in the prairie area of Canada are reviewed; including hydrocarbon syntheses from natural gas and coal, and the hydrogenation of coal, heavy crude oils, and bitumen.

3604. WATANABE, M. Equilibrium in the Reduction of Cobaltous Oxide by Carbon Monoxide. Bull. Inst. Phys. Chem. Research (Tokyo), vol. 9, 1930, pp. 676-682 (abs. 62-63, in English); Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 14, No. 262-263, 1930; Chem. Abs., vol. 25, 1931, p. 3224.

Equilibrium CoO(s) + CO = Co(s) + CO₂ was studied by a static method over the range 563°-861°. The observed values of the equilibrium constant $K_p = p_{CO_2}/p_{CO}$ range between 17.4 (at 563°) and 23.2 (at 861°) and agree over the entire range (within 1%) with the following formula, which was derived with the aid of specific heat data: $-RT \ln K_p = \Delta F^\circ = -11544 + 8.06 T \log T - 0.00305 T^2 + 0.00000031 T^3 - 17.65 T$.

3605. WATANABE, S. (R. C. GRASS, ed.) Bench-Scale Studies of the Fischer-Tropsch Synthesis Over Iron, Nickel, and Nickel-Cobalt Catalysts. Bureau of Mines Inf. Circ. 7611, 1951, 26 pp.

Digest of certain phases of Japanese research in the field of synthetic liquid fuel. The potentialities of Ni as a substitute for Co for the synthesis of hydrocarbons from CO and H₂ were investigated. Extended experiments were carried out to determine the durability of Fe catalysts, to study the yield and quality of the products, and to evaluate Fe catalysts as a potential substitute for Co catalysts in the hydrocarbon synthesis. The experimental procedure and the operating data are presented in considerable detail.

WATANABE, S. Synthesis of Benzine by Catalytic Reduction of Carbon Monoxide at Atmospheric Pressure. VI. Consumption of Carbon Monoxide in Passing Through Catalyst Layer. See abs. 3612.

3606. WATANABE, S., AND MORIKAWA, K. Determination of the Activity of Catalysts Which Accelerate the Benzene Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. Jour. Soc. Chem. Ind. (Japan), vol. 36, 1933, B, p. 226; Brennstoff-Chem., vol. 14, 1933, p. 391.

Several catalysts, the composition of which is not specified, were investigated for their utility in the benzene synthesis. Their efficiency was determined in 2 ways. First, the speed of reaction was determined at certain fixed temperatures by a method of F. Thoren (abs. 3399 and 3400). The catalyst is heated carefully with the reaction gas in a closed glass vessel provided with a Hg manometer and the temperature and pressure are read off at short intervals. The speed of reaction is, of course, not accurately determined, but it is close enough to determine at what temperature it changes suddenly. Second, the activity of the various catalysts is determined on the basis of the yields in liquid hydrocarbons obtained with them. The conclusion reached is that the efficiency of a catalyst is higher the lower the temperature at which the catalyst attains the maximum reaction velocity.

3607. WATANABE, S., MORIKAWA, K., AND IGAWA, S. Synthesis of Benzene (Gasoline) From Carbon Monoxide by Means of Catalytic Reduction at Atmospheric Pressure. I. Methods of Synthesis and Analysis. Jour. Soc. Chem. Ind. (Japan), vol. 37, 1934, B, pp. 142-146; Chem. Abs., vol. 28, 1934, p. 5648.

Experimental apparatus and procedure and the catalysts used are described. Experimental results are reported for reductions under the following conditions: (1) 197°, (2) 197° and 203°, and (3) 197° and 228°, with 32.0% CO and 63.8% H₂ in the raw gas for (1) and (2) and 32.7% CO and 64.5% H₂ for (3). The catalysts for the 3 runs had the compositions: Co:Cu:Th=8:1:0.3 for (1), and Co:Cu:Th=9:1:2 for (2) and (3). Gasoline yields varied 50-65 mg. per l. of gas for (1), 51-76 mg. per l. for (2) and 36-115 mg. per l. for (3). Material balances for 2 runs are appended.

3608. ———. Synthesis of Benzene From Carbon Monoxide by Means of Catalytic Reduction at Atmospheric Pressure. II. Effect of Temperature Upon Synthesis. Jour. Soc. Chem. Ind. (Japan), vol. 37, 1934, B, pp. 385-389; Brennstoff-Chem., vol. 15, 1934, p. 413; Chem. Abs., vol. 28, 1934, p. 6982.

Plots are presented for yield, % of C, and % of H of the reaction products as functions of the reaction temperature, which show that, for benzene synthesis, it is most desirable to keep the reaction temperature nearly at the optimum temperature, in this case 220°, or somewhat below it, as a small rise above the optimum temperature usually promotes undesirable side reactions. The activity of the catalyst is a function of the

location of the maximum point of the curve of gas contraction versus temperature of reduction, a greater activity being associated with a lower temperature value. The Co catalyst, containing Cu, prepared from the carbonate gave an optimum reduction temperature of 250°-300° and that prepared from the nitrate one of 190°-200°. The temperature rise during synthesis, if too great, may adversely affect the activity of the catalyst.

3609. ———. Synthesis of Benzene (Gasoline) From Carbon Monoxide by Catalytic Reduction at Atmospheric Pressure. III. Influence of the Gas Velocity. Jour. Soc. Chem. Ind. (Japan), vol. 38, 1935, B, pp. 70-73; Chem. Abs., vol. 29, 1935, p. 3495.

Yields of gasoline and water per l. of gas decreased with an increase in gas velocity from 0.82 to 2.46 l. per hr., at a temperature of 197°, CO:H₂=33.1:64.7 and 1.33 gm. of catalyst (Co:Cu:ThO₂=9:1:2). At velocities up to 1.13 l. per hr., the rate of gas contraction and the yields of H₂O, CO₂, and gaseous hydrocarbons became constant, whereas the gasoline yield continued to decrease. The optimum gas velocity, which seemed to depend upon the activity of the catalyst, was found to be 1.1 l. per hr. for 1 gm. of catalyst. Higher gas velocities resulted in an increased density of the product. The catalytic reaction was influenced only very slightly by changes in the gas velocity but considerably by temperature changes. Experimental data are reported with 5 refs.

3610. ———. Synthesis of Benzene From Carbon Monoxide by Means of Catalytic Reduction at Atmospheric Pressure. IV. Influence of the Mixing Ratio of Carbon Monoxide and Hydrogen. Jour. Soc. Chem. Ind. (Japan), vol. 38, 1935, B, pp. 328-331; Chem. Abs., vol. 29, 1935, p. 6401.

Ratio H₂:CO was varied from 0.97:1 to 2.96:1. The experimental data are reported. When CO is present in excess of the optimum ratio of CO:H₂=1:2, the production of gaseous olefins and CO₂ is accelerated, but that of gaseous paraffins is retarded. When an excess of H₂ is present, the reverse is the case. The oil production is increased with increasing CO concentration. A theoretical explanation of the reaction mechanism is attempted. Dilution of the raw gas with N₂ increased gaseous olefins and CO₂ and decreased the oil production owing to lowering of the partial pressure of CO.

3611. ———. Synthesis of Benzene by Catalytic Reduction of Carbon Monoxide at Atmospheric Pressure. V. Effect of Adding Lower Hydrocarbons to the Feed Gas. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 967-971; Chem. Abs., vol. 43, 1943, p. 2406.

Fischer synthesis was carried out with 2 vol. CO and 1 vol. H₂ mixed with 8-13% hydrocarbon, and the result was compared with that for feed gas having no admixture. A catalyst of composition of Co:Cu:ThO₂=9:1:2 was used. When the feed gas contained saturated hydrocarbons, the rate of consumption of CO and the formation of CO₂ were lowered and the formation of olefins was slightly increased. With an increase in molecular weight of the added saturated hydrocarbons the number of C atoms in the gaseous saturated hydrocarbons formed was increased. When the feed gas contained unsaturated hydrocarbons, the consumption of CO was lowered but the production of oil was not decreased, about 50% of olefin added being hydrogenated and 30% taking part in polymerization. C₂H₄ yielded a liquid product by self-polymerization.

3612. WATANABE, S. Synthesis of Benzene by Catalytic Reduction of Carbon Monoxide at Atmospheric Pressure. VI. Consumption of Carbon Monoxide in Passing Through Catalyst Layer. Jour. Soc. Chem. Ind. (Japan), vol. 46, 1943, pp. 1128-1130; Chem. Abs., vol. 43, 1943, p. 2406.