about one-half.[91] If the carbon dioxide is to be removed before the Fischer-Tropsch synthesis, it should be removed before the carbon adsorption step, which would make the carbon process even more attractive.

By first removing selectively the bulk of the hydrogen sulfide from raw synthesis gas, then removing the residual hydrogen sulfide with iron oxide, and finally removing all organic sulfur compounds with activated carbon, it is possible to reduce the sulfur content of synthesis gas to less than 0.1 grain per 100 s.c.f. During most of the pilot plant runs, the sulfur content of the purified synthesis gas was less than 0.05 grain per 100 s.c.f.

SYNTHETIC LIQUID FUELS BY GAS SYNTHESIS: RESEARCH AND DEVELOPMENT

Mechanism of the Synthesis

A generalized relationship was developed between reaction rates and the thermodynamics of a system near equilibrium.[92] Equations were derived by which the magnitude of the forward (or backward) reaction rate at equilibrium may be determined from the net reaction rate close to equilibrium. These equations may be used in the study of catalytic processes, such as the water-gas shift reaction, important in the Fischer-Tropsch synthesis, and in the study of homogeneous gas reactions, such as those which occur in rocket nozzles.

For an understanding of the mechanism of the Fischer-Tropsch synthesis and for an estimate of the relative amounts of the products, the product distribution must be known or predictable. The products of the synthesis are not in thermodynamic equilibrium with respect to the types of molecules, structures of the carbon chains, and possibly carbon number distribution. Hence the nature of the products is at least partly determined by the reaction mechanism. Simple rules for stepwise carbon addition predict satisfactorily the experimentally determined hydrocarbon isomer and carbon number distributions in products obtained with cobalt and iron catalysts.[93] According to this mechanism, addition can occur only at end or penultimate carbon atoms of the longest carbon chain and is not possible on a penultimate carbon already attached to three carbon atoms.

Studies of Catalysts

Metallic Carbides

A series of isothermal decompositions of nickel carbide was made in the study of carbon deposition on catalysts.[94] Samples of pure nickel were carburized with carbon monoxide to form nickel carbide, Ni_3C. This was heated at constant temperature, and the course of the decomposition was followed by measuring the increase in ferromagnetism. An induction period preceded the decomposition as shown in figure 19.

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[91] Sands, A. E., Wainwright, H. W., and Egleson, G. C., Organic Sulfur in Synthesis Gas: Occurrence, Determination, and Removal: Bureau of Mines Rept. of Investigations 4699, 1950, 51 pages; Proc. Am. Gas Assoc., 1950, pp. 564-602.

[92] Manes, M., Hofer, L.J.E., and Weller, S., Classical Thermodynamics and Reaction Rates Close to Equilibrium: Jour. Chem. Phys., vol. 18, October 1950, pp. 1355-1361.

[93] Anderson, R. B., Friedel, R. A., and Storch, H. H., Fischer-Tropsch Reaction Mechanism Involving Stepwise Growth of Carbon Chain: Jour. Chem. Phys., vol. 19, March 1951, pp. 313-319.

[94] Hofer, L.J.E., Cohn, E. M., and Peebles, W. C., Isothermal Decomposition of Nickel Carbide: Jour. Phys. Colloid Chem., vol. 54, November 1950, pp. 1161-1169.

There was no detectable change in the structure of the carbide during the induction period, that is, it decomposed into metallic nickel and carbon without the formation of an intermediate carbide. For the period of the decomposition indicated by the linear portion of the curve in figure 19, the reaction was of zero order. Shortening the induction period by temporary overheating did not affect the zero-order rate of the decomposition, except when the normal induction period was completely suppressed, when the zero-order rate was approximately doubled.

Iron is more important as a catalyst for the synthesis of liquid fuels than cobalt or nickel because of lower cost and added flexibility of the syntheses. The iron carbides are almost always formed in the synthesis. The mode of transition from one carbide to the other in the reaction

$$\underset{\text{Hägg carbide}}{3Fe_2C} \longrightarrow \underset{\text{Cementite}}{2Fe_3C} + \underset{\text{Free carbon}}{C}$$

was studied on Hägg carbide, prepared from a precipitated iron catalyst, by successive heat treatments at 525° C. for increasing periods of time.[95] After each treatment the sample was cooled rapidly to 300° C. to suppress further reaction, then cooled very slowly in the range of the magnetic transformations while magnetic measurements were made at frequent intervals. The reaction was found to be a discontinuous precipitation. Hägg carbide and cementite evidently have narrow ranges of composition and do not form intermediate metastable solid solutions. The reaction

$$\underset{\text{Hägg carbide}}{Fe_2C} + Fe \longrightarrow \underset{\text{Cementite}}{Fe_3C}$$

produces cementite in better yields than previously known methods of preparation, and the cementite is pure, unsintered, and suitable for use in the Fischer-Tropsch synthesis.[96] This reaction requires substantially lower temperatures than any other known series of reactions producing cementite and is relatively simple to carry out. When a mixture of Hägg carbide and iron was heated in vacuum to about 450° C. and held at that temperature, the reaction went almost to completion in 1.5 hours.

Analysis of Iron Catalysts

A convenient method for the analysis of used iron catalysts was developed[97] in which the use of thermomagnetic measurements, made with the magnetic balance, in connection with X-ray diffraction and chemical analyses gave data from which the relative amounts of the ferromagnetic phases could be calculated. About 30 percent of the catalyst could not be accounted magnetically. This portion of unknown composition may result from magnetic unsaturation, and some may be finely divided or in an otherwise magnetically hard state. This latter may play a part in the synthesis.

The relative amounts of iron and its compounds were determined as a function of catalyst life by the magnetic method.[98] The catalyst was periodically removed and

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[95] Cohn, E. M., and Hofer, J. J. E., Mode of Transition from Hägg Iron Carbide to Cementite: Jour. Am. Chem. Soc., vol. 72, October 1950, pp. 4662-4664.

[96] Cohn, E. M., and Hofer, L. J. E., Preparation of Iron Carbides: U. S. Patent 2,535,042, December 1950.

[97] Hofer, L. J. E. and Cohn, E. M., Thermomagnetic Determination of Hägg Carbide in Used Iron Fischer-Tropsch Catalysts: Anal. Chem., vol. 22, July 1950, pp. 907-910.

[98] Anderson, R. B., Hofer, L. J. E., Cohn, E. M., and Seligman, B., Studies in the Fischer-Tropsch Synthesis. IX. Phase Changes of Iron Catalysts in the Synthesis: Jour. Am. Chem. Soc., vol. 73, March 1951, pp. 944-946.

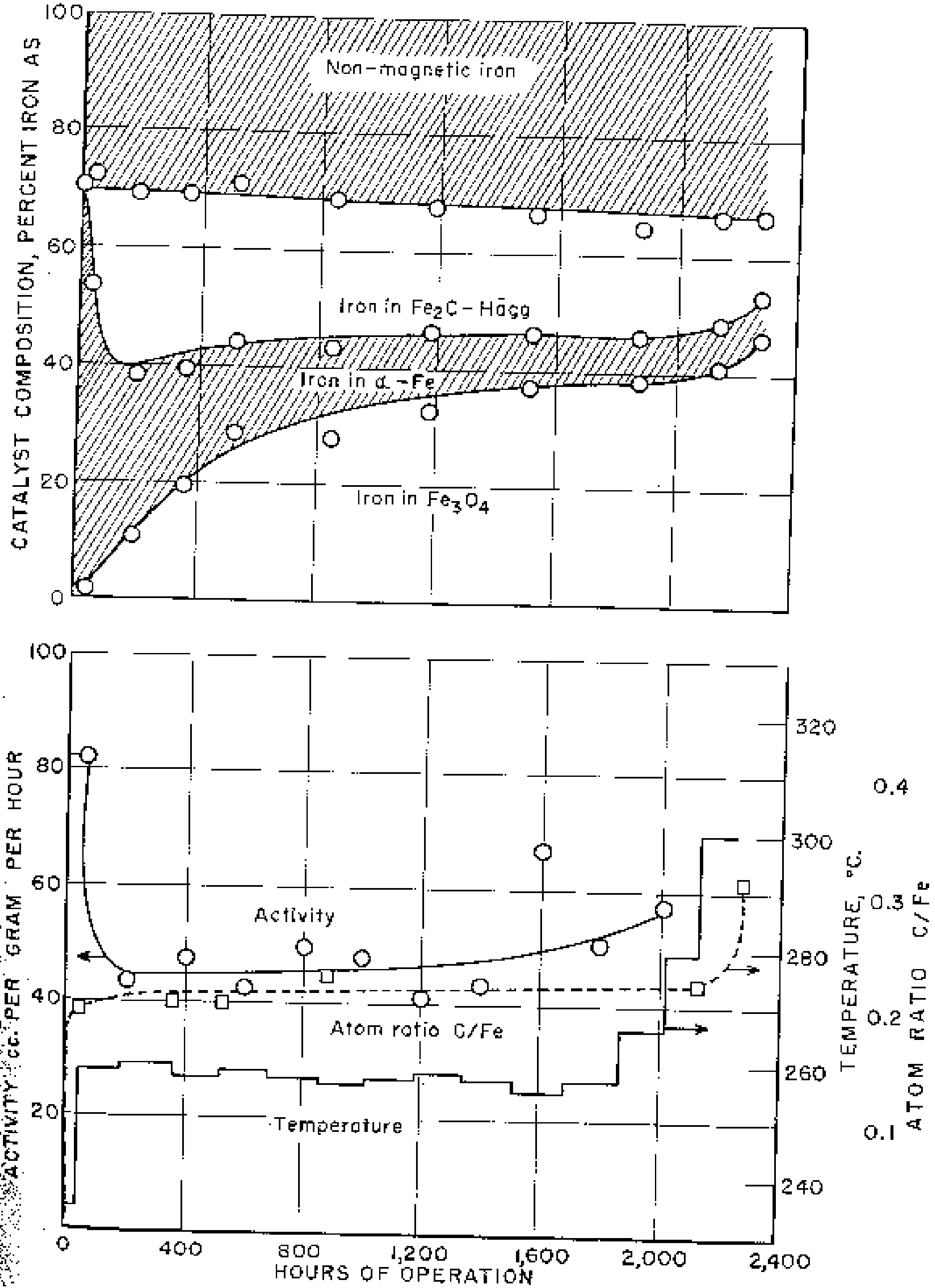

Figure 20. - The variation of catalyst composition, activity, and temperature with time: Fe_3O_4-MgO-K_2O catalyst at 7.8 atmospheres of $1H_2 : 1CO$ gas.

sampled, care being taken to avoid its exposure to the atmosphere. The original reduced catalyst contained only metallic and "nonmagnetic" iron. As shown in figure 20, the amount of the latter remained essentially constant at about 30 percent throughout the synthesis. While the amount of metallic iron decreased continuously, Hägg carbide formation reached a maximum in about 8 days, after which it was oxidized at a considerably slower rate than iron.

Nitrided Iron Catalysts

Treating iron with ammonia to convert it to iron nitride resulted in catalysts of enhanced activity and longer life that produced large amounts of oxygenated products.[99] Depending on the ammonia treatment, various iron nitrides are formed. These are interstitial compounds similar to, and in some cases isomorphous with, the carbides of iron.

Nitrided fused catalysts operated at a considerably lower temperature than the same reduced catalysts. In a life test one nitrided catalyst operated for 190 days at 7.8 atmospheres; at the end of that time the temperature of operation was below that of a reduced catalyst, and the catalyst was still in good condition. Tests with initially reduced catalysts were usually ended in much shorter periods because of oxidation or plugging of the catalyst bed by carbon or wax deposits. The operation of nitrided catalysts at 21.4 atmospheres pressure was characterized by nearly constant temperature of operation, but the increase in activity over that of the reduced catalyst was not as marked as for the operation at 7.8 atmospheres. Greater yields of gaseous hydrocarbons and oxygenated compounds, including alcohols, were obtained with nitrided catalysts than with reduced catalysts. The difference in selectivity must be related to a specific change of the catalyst surface. The tendency of nitrided catalysts to resist oxidation and free carbon deposition may contribute to the longer life of these catalysts.

Surface Area and Pore Volume Studies

As part of the research on the changes that occur in iron catalysts during pretreatment or during synthesis, the changes in surface areas and pore volumes of a precipitated and of a fused iron catalyst have been investigated.[1] The two catalysts differed widely in their original form, the precipitated catalyst, being a ferric oxide gel, had a high surface area before reduction, while the unreduced fused-iron oxide catalyst had a small surface area. After reduction in hydrogen, the two catalysts had similar surface areas (6-10 $m.^2$/gm.) and pore volumes (.09-.16 cc./gm.).

When the precipitated catalyst was sintered in nitrogen at increasing temperatures up to 550° C., the pore volume reached a maximum of 0.151 cc./gm. at 300° C. and then decreased, while the surface area decreased progressively. The average pore diameter increased with increasing sintering temperatures. Reduction of the fused catalyst resulted in an increase in surface area because of the removal of oxygen, although the external volume did not change. Up to 90 percent reduction, the pore volume and surface area increased linearly with extent of reduction.

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[99] Anderson, R. B., Shultz, J. F., Seligman, B., Hall, W. K., and Storch, H. H., Studies of the Fischer-Tropsch Synthesis. VII. Nitrides of Iron as Catalysts: Jour. Am. Chem. Soc., vol. 72, August 1950, pp. 3502-3508.

[1] Hall, W. K., Tarn, W. H., and Anderson, R. B., Studies of the Fischer-Tropsch Synthesis. VIII. Surface Area and Pore Volume Studies of Iron Catalysts: Jour. Am. Chem. Soc., vol. 72, December 1950, pp. 5436-5443.

When the reduction temperature was increased to 650° C., the surface area was reduc to about one-sixth of the area of the same catalyst reduced at 450° C., and the ave age pore diameter increased eightfold. At 650° C. the promoters still retarded but could not prevent sintering of the newly developed surface, as they had at lower temperatures. The reduced fused catalysts had higher surface areas than reduced pure magnetite. For preparations of this type, variation of the reduction temperature affords a method for producing catalysts with predetermined pore diameters. This effect may be of considerable practical importance, as the activity of the catalyst is related to the pore diameter.

Pilot-Plant Developments

Oil-Circulation Processes

Bureau of Mines developments in the oil-circulation Fischer-Tropsch process have been to improve existing processes by eliminating the features that cause catalyst disintegration and cementing.[2] The moving catalyst bed, developed to eliminate the cementing problem in fixed-catalyst beds, operated for several months without an increase in pressure drop across the bed and without cementing of the catalyst. The apparatus and controls are shown in figure 21. Decrease in catalyst activity and carry-over of catalyst into the oil-circulation lines were negligible. Other advantages of the moving bed over the fixed-bed process were found to be: Greater catalyst activity per unit mass due to the use of finer particles (that is, due to larger geometric surface area per weight of catalyst); lower operating temperatures; and easier charging and withdrawal of catalyst. A 91 percent over-all synthesis-gas conversion is obtainable, using 1.3:1 hydrogen to carbon monoxide synthesis gas, by operating a two-stage process with 70 percent conversion in each stage and with a recycle ratio of tail gas to fresh synthesis gas of 1:1. A rapid decline in catalyst activity occurred when 25 percent carbon dioxide was added to the feed gas to simulate operation of a second stage without removal of carbon dioxide. No attempt was made to determine the maximum catalyst life, but it was noted that one batch of catalyst still possessed considerable activity after about 2,700 hours of synthesis.

As compared with fixed-bed runs, the moving-bed experiments yielded smaller amounts of gaseous hydrocarbons and oxygenated products. The gas recycle ratio (volume of tail gas to fresh gas) was varied to study the effect on the usage ratio (volume of hydrogen reacted per volume of carbon monoxide) of synthesis gas and on the production of hydrocarbon gas. As the recycle ratio increased, the gas production decreased, and the hydrogen to carbon monoxide usage ratio rose. Both of these trends are desirable for efficient conversion of synthesis gas.

Feed gas with a hydrogen to carbon monoxide ratio of 1:1 can be used. This is more economically produced from coal than hydrogen-rich gas and may offer the best possibility for achieving more economical synthesis gas usage, as the cost of purified synthesis gas, produced from coal, has been estimated to be about 60-70 percent of the total cost of the synthesis.

Slurry-Phase Operation

In the slurry-phase method for the Fischer-Tropsch synthesis, finely divided catalyst is suspended in oil, and the reaction gas is bubbled through the oil at a

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[2] Crowell, J. H., Benson, H. E., Field, J. H., and Storch, H. H., Fischer-Tropsch Oil Circulation Processes: Ind. Eng. Chem., vol. 42, November 1950, pp. 2376-2384.

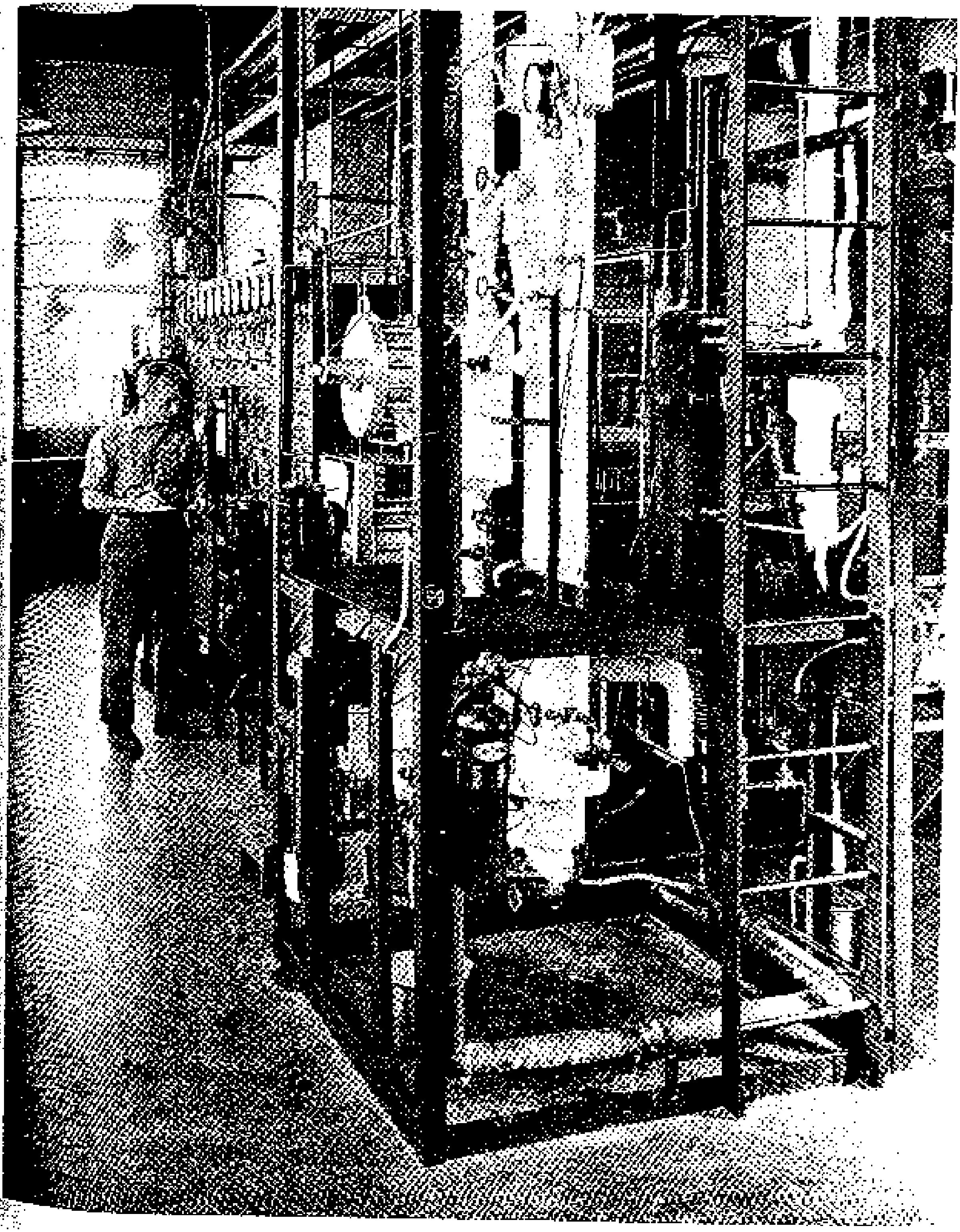

Figure 21. - Large catalyst-oil slurry unit.

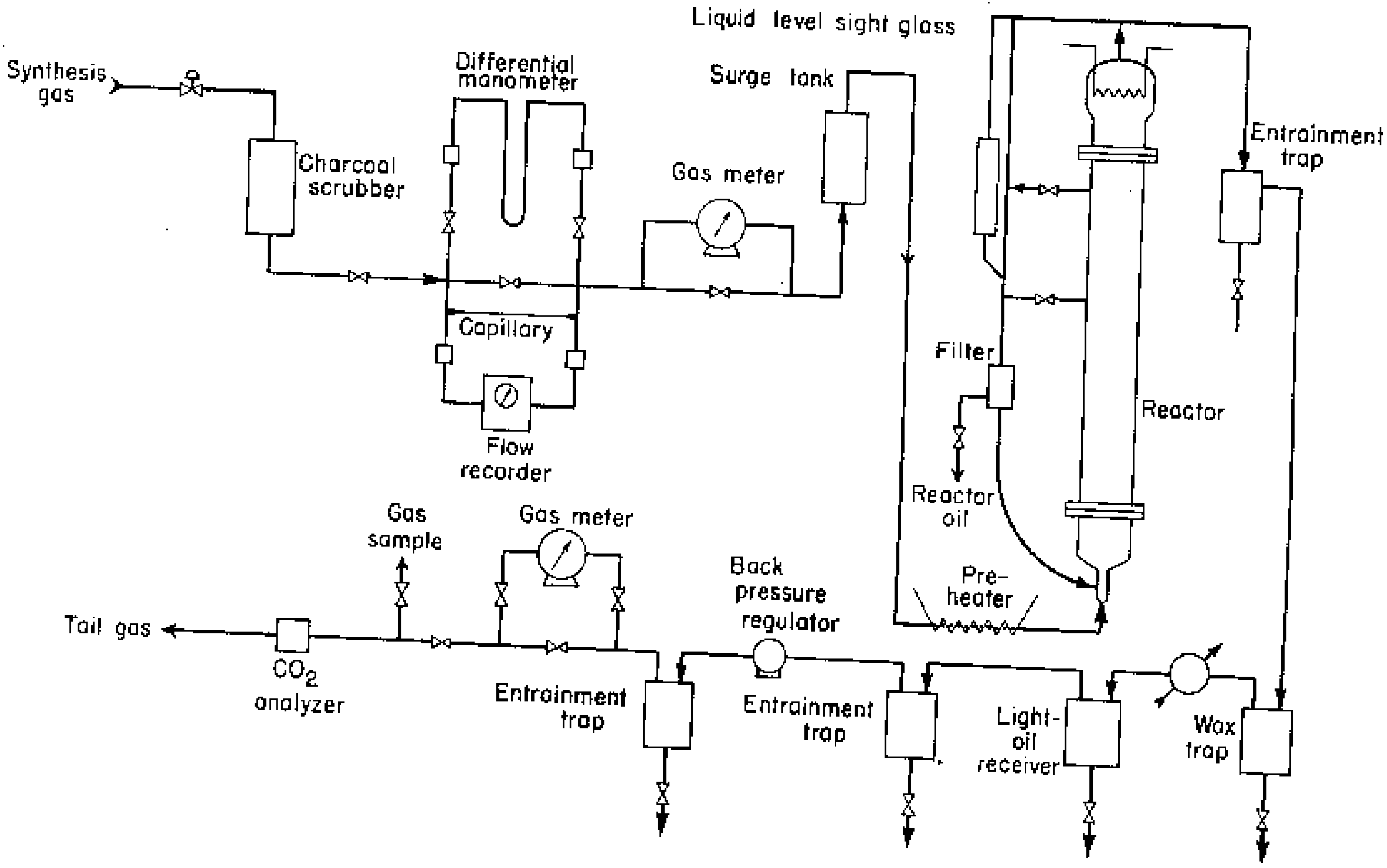

Figure 22. - Flow diagram of oil slurry process.

rate rapid enough to keep the catalyst in suspension. Orienting pilot-plant tests in a circulating system, as diagramatically shown in figure 22, were made with a copper- and potassium-promoted precipitated iron catalyst.[3] During the operation, which lasted for 75 weeks, the pressure was varied from 100 to 250 p.s.i.g., the space velocity from 130 to 300, and the temperature from 242° to 276° C. The activity declined steadily during the test, requiring increases in temperature or pressure to compensate for the deactivation. Catalyst settling was a contributing mechanical cause for decreased activity, as was found by the determination of the slurry densities at different bed heights and time intervals. A slow, continuous increase in the carbon content of the catalyst was observed.

The production of light hydrocarbons increased with temperature. Pressure had a negligible influence on the extent of methane formation but augmented the carbon monoxide conversion, especially below 200 p.s.i.g.

The over-all conversion of synthesis gas was 55 percent, resulting in average yields of 12 gm. (per cubic meter of inlet gas) of gaseous hydrocarbons ($C_1 + C_2$), 90 gm. of C_3 and higher hydrocarbons, and 12 gm. of water. The average wax content (fraction boiling above 450° C.) of the slurry was more than 50 percent. Of the reacted carbon monoxide, 5 percent was converted to $C_1 + C_2$, 43 percent to C_3 and heavier, and 42 percent to carbon dioxide. About 10 percent of the carbon monoxide was unaccounted, partly because no detailed analysis of oxygenated compounds was made.

Fixed- and Fluidized-Bed Studies

To obtain engineering data on the flow of gases through beds of catalysts, preliminary investigation of the physical phenomena of elutriation was made,[4] using mixtures of particles of different diameters, the coarser particles serving as "solvent" and the fines as "solute." Within certain ranges of concentration of fines in fluidized mixtures of sand and of fused iron catalyst,

$$c = c_o e^{-2.303\ kt},$$

where c was the concentration of fines at time t, c_o was the initial concentration of fines, and k was a quasi-first-order specific reaction rate constant. This elutriation rate constant was rather insensitive to changes in the composition and range of sizes of the "solvent," but it increased rapidly with increasing average diameter and decreasing density of the "solute." Within the range of conditions tested, it varied directly with the fourth power of the linear rate of gas flow.

Heat transfer in packed tubes was studied with equipment having high ratios of particle to tube diameter[5] and the following empirical correlation was found:

$$\frac{Nu'}{Re^{0.75}} = 0.125,$$

where Nu' is the modified Nusselt number, and Re is the modified Reynolds number.

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[3] Schlesinger, M. D., Crowell, J. H., Leva, M., and Storch, H. H., Fischer-Tropsch Synthesis in the Slurry Phase: Ind. Eng. Chem., vol. 43, June 1951, pp. 1474-1479.

[4] Leva, M., Elutriation of Fines from Fluidized Systems: Chem. Eng. Progress, vol. 47, January 1951, pp. 39-45.

[5] Leva, M., Packed Tube Heat Transfer: Ind. Eng. Chem., vol. 42, December 1950, pp. 2498-2501.

Within experimental limits, the tube diameter had no effect upon the heat-transfer coefficients, which were surprisingly high as compared with those predicted by a correlation based on small ratios of particle size to tube diameter. Increasing the particle size caused a significant reduction in pressure drop, and the heat-transfer to pressure-drop relationship agreed with available data. A qualitative evaluation of the wall effect showed that fluid channeling between catalyst bed and wall (and thus catalyst by-passing) became increasingly severe as the ratio of particle diameter to tube diameter increased. Therefore, the use of high ratios is undesirable for contact catalysis where contact between solid and gas and effective utilization of the latter are of prime importance.

Production of Alcohols

In the reaction, wherein an alcohol is treated with synthesis gas (carbon monoxide and hydrogen) in the presence of a cobalt catalyst to produce a primary alcohol containing one more carbon atoms than the starting material, the order of reactivity is usually tertiary > secondary > primary. However, methyl alcohol is anomalous in that it reacts with synthesis gas more rapidly than do secondary alcohols.[6] The chief product of this reaction is ethyl alcohol, which can be homologated further only with difficulty. This method of making ethanol is not only of technical interest but is also of theoretical value, as the reaction cannot proceed via an olefin intermediate. Furthermore, the product distribution from this reaction was similar to that of the oxygenated fraction of Fischer-Tropsch synthesis products.

Higher alcohols can be obtained from aldehydes and ketones[7][8][9] by the same type of reaction. The catalysis appears to be homogeneous and to go by way of cobalt hydrocarbonyl or dicobalt octacarbonyl, as it is not affected adversely by sulfur compounds, which inhibit hydrogenation on a solid catalyst. In systems containing conjugated double bonds, both hydrogenation and hydroformylation occur. The former becomes the dominant reaction as the degree of double-bond character of an olefinic linkage diminishes because of conjugation. There must be adequate concentration of carbon monoxide in the reacting mixture to form cobalt carbonyl. If the partial pressure of carbon monoxide is below this threshold value, the cobalt metal may be poisoned for any catalytic activity or - in the absence of carbon monoxide - heterogeneous hydrogenation on metallic cobalt may proceed.

Oxygen Exchange Between Nitrates and Water

In a cooperative project with the Explosives and Physical Sciences Division, Region VIII, the mass spectrometer was used for the analysis of the oxygen exchange between nitrates and water.[10] Water enriched with O^{18} exchanged its tagged oxygen with a 40-percent solution of nitric acid at 30° C., but did not undergo exchange with cellulose nitrate 1N sulfuric acid solution at 23° and 100° C., as determined by analysis of the water.

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[6] Wender, I., Friedel, R. A., and Orchin, M., Ethanol from Methanol: Science, vol. 113, February 1951, pp. 206-207.

[7] Wender, I., Levine, R., and Orchin, M., Chemistry of the Oxo and Related Reactions. II. Hydrogenation: Jour. Am. Chem. Soc., vol. 72, October 1950, pp. 4375-4378.

[8] Wender, I., Orchin, M., and Storch, H. H., Mechanism of the Oxo and Related Reactions. III. Evidence for Homogeneous Hydrogenation: Jour. Am. Chem. Soc., vol. 72, October 1950, p. 4842.

[9] Wender, Irving, Greenfield, Harold, and Orchin, Milton, Chemistry of the Oxo and Related Reactions. IV. Reductions in the Aromatic Series: Jour. Am. Chem. Soc., vol. 73, No. 6, June 1951, pp. 2656-2658.

[10] Klein, R. and Friedel, R. A., Oxygen Exchange Between Nitrates and Water: Jour. Am. Chem. Soc., vol. 72, August 1950, pp. 3810-3811.

Batch Autoclave Studies

Mechanism of Coal Hydrogenation

A study[11] in small autoclaves of the hydrogenation and pyrolysis of anthraxylon from bituminous coal has been made as part of the program to elucidate the mechanism of coal hydrogenation. Table 14 shows the product distribution for hydrogenation and pyrolysis of anthraxylon, where the hydrogenation was carried out in a hydrogen atmosphere and the pyrolysis in a nitrogen atmosphere. In the absence of catalyst, the conversion of anthraxylon to asphalt, gas, and oil was very low. The carbon dioxide formation was small, yet greater than in the presence of catalyst (1 percent tin plus 0.5 percent ammonium chloride). Elimination of oxygen as water and extent of liquefaction were increased by the presence of a catalyst. However, the amount of liquefaction alone does not determine the degree of oxygen elimination. Apparently, liquefaction is always accompanied by the formation of a large amount of water, but the converse is not true.

TABLE 14. - Product distributions for hydrogenation and pyrolysis of anthraxylon[1]

Run No.	Temperature, °C.	Catalyst	Hydrogenation							
			Moisture and ash-free coal, percent							
			Organic benzene-insolubles	Asphalt	Oil	Hydrocarbon gases	CO_2	H_2S	H_2O	H_2 absorbed
1,180.....	400	-	89.75	2.57	2.98	2.37	0.82	0.10	1.21	0.03
1,320.....	400	[2]	24.89	61.01	8.13	4.63	.51	.10	3.82	2.54
1,284.....	450	-	73.16	5.66	7.62	8.23	1.13	-	3.21	.66
1,219.....	450	[2]	13.96	40.84	28.09	12.96	.20	.10	5.72	3.37
			Pyrolysis							
1,193.....	400	-	92.83	-	2.88	2.12	0.72	0.10	1.29	-0.32
1,191.....	400	[2]	91.46	-	2.88	2.16	.62	-	.71	- .73
1,206.....	450	-	88.33	-	4.94	3.12	1.13	-	1.59	- .56
1,192.....	450	[2]	86.93	-	4.73	3.60	1.13	-	2.08	- .69

[1] 100 gm. Bruceton anthraxylon, 1 hr., 1,000 lb./in.^{2} initial hydrogen or nitrogen pressure.

[2] 1 percent tin plus 0.5 percent ammonium chloride.

The first step in the over-all hydrogenolysis of coal may be a splitting reaction resulting in reactive fragments. These fragments can either be stabilized by adding hydrogen to form benzene-soluble products or they can be polymerized, without hydrogenation, to form benzene-insoluble products. The results of an uncatalyzed run tend to support this hypothesis, as low hydrogen consumption, low production of water and hydrocarbon gas, and high production of benzene-insolubles were observed. The small extent of liquefaction obtained with anthraxylon under these conditions may be interpreted as resulting from a slow rate of hydrogenation of fragments compared to their rate of polymerization. If the theory is correct, the production of much of the water and of hydrocarbon gas during coal hydrogenation must be associated with some process other than the first step in which reactive fragments are formed.

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[11] Pelipetz, M. G., Weller, S., and Clark, E. L., Hydrogenation and Pyrolysis of Anthraxylon from Bituminous Coal: Fuel, vol. 29, September 1950, pp. 208-213.

The above hypothesis was further substantiated by studying the pyrolysis of coal under the same conditions and in the same equipment as used for hydrogenation, but with a nitrogen atmosphere instead of hydrogen. As shown in table 14, only small amounts of gas, water, and oil were formed, and virtually no asphalt was produced. The course of the pyrolysis was essentially unaffected by the presence of a catalyst, and the effect of temperature was small. As primary splitting appears to take place in the same temperature range during pyrolysis, these data support the assumption that much of the water and gas production results from secondary reactions. The former probably is the result of the reaction of oxygen-containing groups with gaseous hydrogen.

Catalysts for Coal Hydrogenation

The activity of a number of catalysts was much greater when they were impregnated on the coal from aqueous solution than when they were added as powders to powdered coal.12/13/ Ball-milling of coal and catalyst together was of intermediate effectiveness. Thus, if the catalyst is evenly distributed throughout the coal, the efficiency of many hydrogenation catalysts can be significantly improved, and cheaper and more readily available catalysts utilized. The unique position of tin compounds as hydrogenation catalysts no longer exists, and the explanation of their high activity in powdered form must be sought in an as yet unknown mechanism, which permits good distribution of tin compounds, regardless of the form in which they are added.

Pilot-Plant Construction: Vapor-Phase Hydrogenation Unit

To provide equipment for the hydrogenation of oils over a fixed catalyst bed, a small plant suitable for operation at 500° C. and 10,000 p.s.i.g. has been designed.14/ A simplified flow diagram of the unit is shown in figure 23. Special connections and valves were designed for the unit. All high-pressure equipment, except compressor and pump, was enclosed in an open-topped stall with concrete walls. The performance of the unit was tested, using an aromatic oil (boiling below 325° C.) as the raw material. This was obtained by distillation of a blend of light oils originating from coal that had been hydrogenated in the liquid-phase. Product analyses and material balances indicated that a catalyst consisting of small amounts of chromium, molybdenum, and zinc oxides deposited on fuller's earth activated with hydrogen fluoride was suitable for the hydrogenation, in the course of which the oxygen sulfur, and nitrogen contents were reduced. The gasoline produced, which was approximately 50 percent of the starting material, retained the original aromatic structure and possessed good antiknock characteristics. The results indicated the suitability of the plant for performing high-pressure catalytic reactions.

Separation and Identification of Products of Coal Hydrogenation

X-Ray Diffraction Analysis

Solid crystalline, aromatic hydrocarbons can be identified by X-ray diffraction powder patterns, in which closely related compounds, even isomers, can be distinguished,

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12/ Weller, S. and Pelipetz, M. G., Coal-Hydrogenation Catalysts. Studies of Catalyst Distribution: Ind. Eng. Chem., vol. 43, May 1951, pp. 1243-1246.

13/ Weller, S. and Pelipetz, M. G., Catalysis in Liquid-Phase Coal-Hydrogenation: Proc. Third World Petrol. Cong., The Hague, Netherlands, sec. IV, subsec. I, preprint 7, June 3, 1951, 6 pp.

14/ Wolfson, M. L., Pelipetz, M. G., Damick, A. D., and Clark, E. L., Vapor-Phase Hydrogenation of Light and Heavy Oils: Ind. Eng. Chem. vol. 43, February 1951, pp. 536-540.

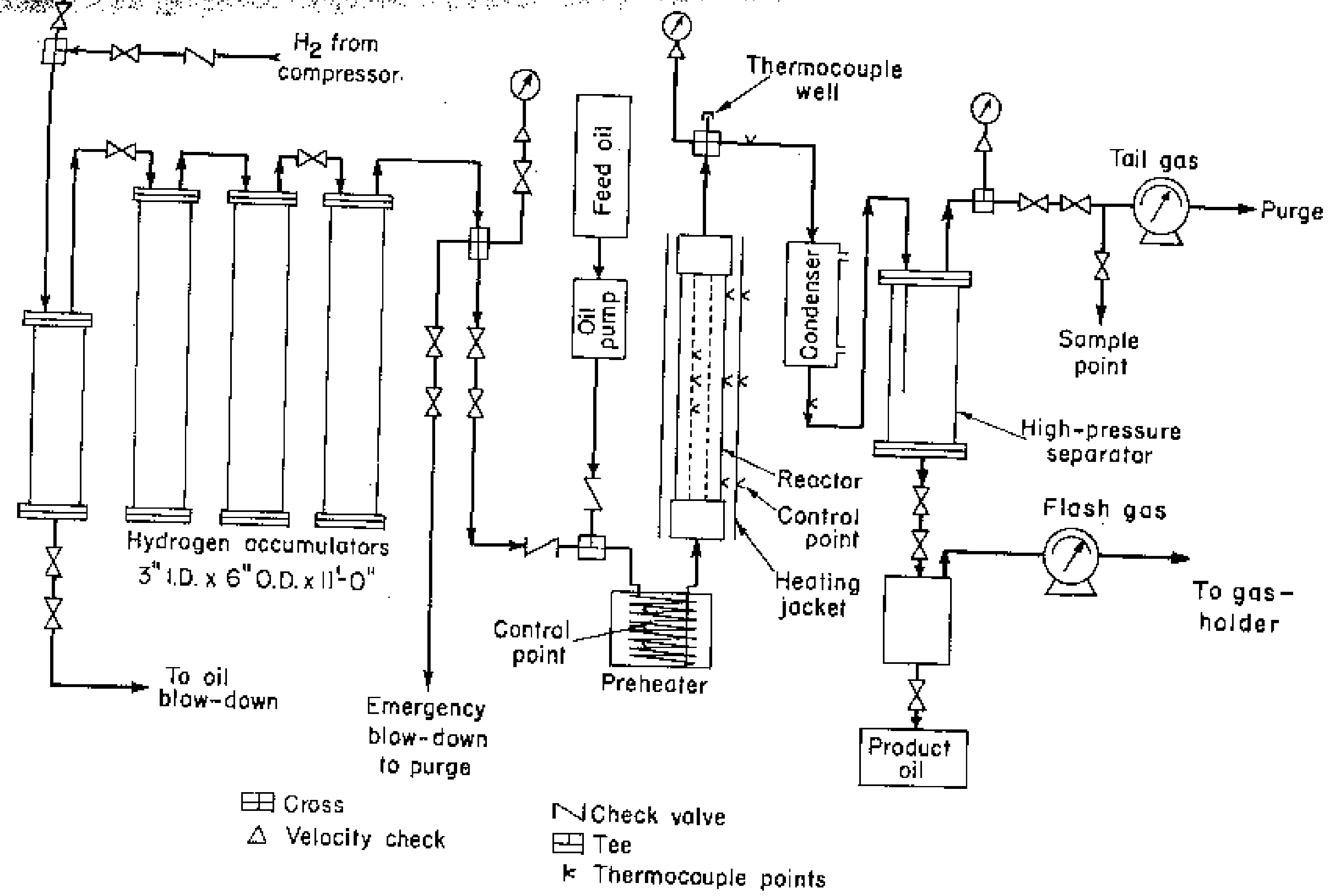

Figure 23. - Flow diagram of vapor-phase hydrogenation unit.

while impurities adequate to lower the melting point by as much as 15° C. do not appreciably modify the patterns.[15] A sample-preparation method was developed,[16] and the patterns of 59 hydrocarbons were obtained. The method is applicable to microsamples and is nondestructive.

Studies of Phenols in Coal-Hydrogenation Oils

A study of the tar acids in coal-hydrogenation oils[17] deals with their potential commercial importance, occurrence, and separation. The tar-acid fraction of the n-hexane-soluble portion of the liquid product obtained by the hydrogenation of Pittsburgh-bed (Bruceton) coal was isolated by methanolic alkali extraction of the benzene solution of the oil. The yield of tar acids was 9.4 percent by weight of the n-hexane-soluble oil, or 5.2 percent of the total oil produced in the hydrogenation. The tar acids were subjected to distillation, and 136 fractions were collected. The refractive index of each fraction and the densities of the higher-boiling fractions were determined. Careful interpretation of the data on physical constants makes it possible to select those fractions that are rich in any desired phenol known to occur in the oil. A study of the distribution (partition) of various phenols between cyclohexane and a buffered aqueous phase led not only to the development of rules and formulas relating partition coefficient to ionization constant but also to a more complete understanding of the factors governing the extractability of phenols. The differences in partition coefficients of isomeric phenols permitted the application of the countercurrent distribution method to their separation and determination of purity. The infrared spectra of many phenols of known constitution were determined,[18] and this information was applied to the qualitative and quantitative estimation of the composition of most of the tar-acid fractions. The ultraviolet absorption spectra of all the phenols known to occur in the oil obtained from the hydrogenation of coal were determined. The more classical methods of organic chemistry, such as crystallization, preparation of derivatives, and degradative studies, also were used. Chemical and physical investigation of the various fractions resulted in the identification of 16 individual phenols, as well as inconclusive evidence of the presence of 2 others, as shown in table 15.

Partition Studies

A satisfactory method that involves a means of increasing the concentration of solute in one of the solvents was developed[19] for measuring large or small partition coefficients to obtain measurable amounts of solute. The technique, interchange extraction, was subjected to precise mathematical analysis. The distributions of pyridine, quinoline, and certain of their methyl-substituted derivatives were studied in immiscible systems composed of cyclohexane or chloroform and of water or citrate-phosphate buffer.[20] The data thus obtained will be useful for the separation of isomeric heterocyclic bases by countercurrent distribution.

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[15] Hofer, L. J. E., and Peebles, W. C., X-Ray Diffraction Patterns of Solid Aromatic Hydrocarbons: Anal. Chem., vol. 23, May 1951, pp. 690-695.

[16] Hofer, L. J. E., Peebles, W. C., and Guest, P. G., Preparing Extruded Samples for X-Ray Diffraction Analysis: Anal. Chem. vol. 22, September 1950, pp. 1218-1219.

[17] Woolfolk, E. O., Golumbic, C., Friedel, R. A., Orchin, Milton, and Storch, H. H., Characterization of Tar Acids from Coal-Hydrogenation Oils: Bureau of Mines Bull. 487, 1950, 56 pp.

[18] Friedel, R. A., Infrared Spectra of Phenols: Jour. Am. Chem. Soc., vol. 73, No. 6, June 1951, pp. 2881-2884.

[19] Golumbic, C. and Weller, S., Measurement of Large Partition Coefficients by Interchange Extraction: Anal. Chem., vol. 22, November 1950, pp. 1418-1419.

[20] Golumbic, C. and Orchin, M., Partition Studies. V. Partition Coefficients and Ionization Constants of Methyl-Substituted Pyridines Quinolines: Jour. Am. Chem. Soc., vol. 72, September 1950, pp. 4145-4147.

TABLE 15. - Tar acids found in the oil from hydrogenation of Bruceton coal

Compound	Hexane-soluble oil, percent	Total oil,	Pounds per ton of total oil	Pounds per ton of coal[1]
Phenol	0.24	0.13	2.6	2.0
o-Cresol	.37	.20	4.0	3.1
m-Cresol	.55	.30	6.0	4.7
p-Cresol	.25	.14	2.8	2.2
2,4-Xylenol	.23	.13	2.6	2.0
2,5-Xylenol	.14	.08	1.6	1.2
3,5-Xylenol	.25	.14	2.8	2.2
3,4-Xylenol	.05	.03	.6	.5
2,3-Xylenol[2]	-	-	-	-
o-Ethylphenol	.03	.02	.4	.3
m-Ethylphenol	.42	.23	4.6	3.6
p-Ethylphenol	.09	.05	1.0	.8
Mesitol[2]	-	-	-	-
3-Methyl-5-ethylphenol	.27	.15	3.0	2.3
4-Indanol	.19	.10	2.0	1.6
5-Indanol	.13	.07	1.4	1.1
o-Phenylphenol[3]	-	-	-	-
p-Phenylphenol[3]	-	-	-	-
Total	3.21	1.77	35.40	27.60

[1] Dry, ash-free coal.
[2] Presence indicated by chemical methods, but presence could not be confirmed spectroscopically.
[3] Definitely shown to be present, but quantity not estimated.

The phenolic constituents of asphalt obtained by coal hydrogenation also were examined by the countercurrent-distribution method.[21] As defined here, asphalt is the benzene-soluble, n-hexane-insoluble portion of the coal-hydrogenation product. Two groups of phenols were distinguished: One group, extracted by aqueous alkali, comprised alkyl phenols and phenyl phenols; the other group, soluble only in methanolic alkali, was probably a mixture of polynuclear phenols. The oxygen content of the latter group amounted to about one-third of the total oxygen in the asphalt, most of which was present in hydroxyl groups. Only about 30 percent of the oxygen in the nonextracted fraction could be ascribed definitely to hydroxyl groups.

Organic Syntheses

The synthesis of organic compounds[22][23][24] was continued as part of the program to study the structure of coal and to identify the products of its hydrogenation.

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[21] Fusack, R., and Golumbic, C., The Characterization of the Phenolic Fraction of Coal-Hydrogenation Asphalt: Jour. Am. Chem. Soc., vol. 73, April 1951, pp. 1567-1571.

[22] Orchin, M., Reggel, L., and Friedel, R. A., The Anomalous Reaction of 1-Tetralone with o-Tolylmagnesium Bromide: Jour. Am. Chem. Soc., vol. 73, April 1951, pp. 1449-1454.

[23] Orchin, M., and Reggel, L., Aromatic Cyclodehydrogenation: X. Studies on Ring Oxygen Compounds. Dinaphtho 1, 2, 1', 2' -furan: Jour. Am. Chem. Soc., vol. 73, April 1951, pp. 1877-1878.

[24] Orchin, Milton and Reggel, Leslie, A Synthesis of Fluoranthene by Cyclohydrogenation: Jour. Am. Chem. Soc., vol. 73, No. 6 June 1951, pp. 2955, 2956.

Methods for the preparation of two isomers of benzfluoranthene were developed in another synthesis study.[25]

The distillation laboratory at Bruceton is used for separating and identifying products obtained by the synthetic liquid fuel processes. The laboratory was designed for flexibility and versatility of operation[26] because a large variety of organic compounds must be handled. These were achieved, in part, by standardization of basic equipment, permitting interchange of parts and maximum service.

The effect of pressure and of the type of packing on the efficiency of packed distillation columns was studied by measuring fractionating efficiencies, throughputs, and holdups at various reflux rates.[27] Pressures from 20 to 760 mm.-Hg, with Berl saddles, single- and triple-turn helices, glass spheres, and a commercial Heli-grid column packing, were used. In general, efficiencies decreased with decreasing pressure below about 200 mm.-Hg. The fixed-Heli-grid packing was superior to all of the loose packings that were tested; of the latter, glass spheres gave the best results. Columns filled with loose packings were most efficient when operated near maximum throughput capacity; their highest separating power appears to be near 200 mm.-Hg.

Permeation of Gases Through Membranes

The cost of gas is an important factor in the production of synthetic liquid fuel. Oxygen is needed for the gasification of coal, and hydrogen for use in the synthesis gas mixture or for use in the hydrogenation of coal. One of the most promising methods for the production of these gases, at a cost competitive with commercial methods, is the enrichment of hydrogen or oxygen in gas mixtures by fractional or differential permeation through nonporous membranes. Of 15 nonporous films tested in a laboratory-scale apparatus, natural rubber was outstanding in showing the highest permeability toward the gases tested. Its selectivity as between gases, however, was not as great as that of several other films, and it was subject to oxidation, with consequent change in properties. Ethyl cellulose best satisfies the requirements of high permeability and high selectivity. The permeability of the membranes for each gas tested (nitrogen, oxygen, hydrogen, helium) increased with increasing temperature. The temperature dependence (and therefore the activation energy for permeation) is about the same for oxygen, helium, and hydrogen, but is greater for nitrogen. For the enrichment of gas mixtures, a compromise must be made between the use of higher temperatures to obtain higher permeability and lower temperatures to obtain greater selectivity. The use of a fractional permeation process may be of practical importance[28][29][30] to effect such separations as oxygen from air, helium from natural gas, and hydrogen from hydrogenation tail gas. As the permeable films are not perfectly selective, it is

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[25] Orchin, M., and Reggel, L., Synthesis of Benz [j] Fluoranthene and Benz [k] Fluoranthene: Jour. Am. Chem. Soc., vol. 73, January 1951, pp. 436-442.

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

[27] Myles, M., Feldman, J., Wender, I., and Orchin, M., Fractionating Efficiency of Various Packings: Ind. Eng. Chem., vol. 43, June 1951, pp. 1452-1456.

[28] Weller, S. and Steiner, W. A., Engineering Aspects of Separation of Gases. Fractional Permeation through Membranes: Chem. Eng. Prog., vol. 46, November 1950, pp. 585-590.

[29] Weller, S. and Steiner, W. A., Separation of Oxygen from Gas Mixtures Containing the Same: U. S. Patent 2,540,151, Feb. 6, 1951.

[30] Weller, S., Recovery of Light Elemental Gases: U. S. Patent 2,540,152, Feb. 6, 1951.