This unit was used to determine the activity of a German hydrogenation catalyst for the production of Diesel oil from a blend of light oils (boiling below 325° C.) obtained by hydrogenating various coals in the Pittsburgh pilot-plant operations. This particular catalyst was shown to produce a good aromatic gasoline (boiling point, 200° -325° C.) in single-pass operation, but several passes would be required to produce a usable Diesel oil that requires further saturation of the aromatic constituents.

Separation and Identification of Products of Coal Hydrogenation

The most valuable byproduct fraction from the hydrogenation of coal is the alkali-soluble portion, commonly designated as the tar-acid fraction.[77] This material is a complex mixture of acidic aromatic hydroxy compounds or phenols. Information concerning tar acids produced in the liquid-phase hydrogenation of coal is of considerable engineering and chemical interest, in that the critical reaction in the liquefaction of coal is probably the hydrogenolysis of carbon-to-oxygen bonds, and a study of the structure of the phenolic products should shed light on the constitution of coal. Knowledge of the constitution of these phenols also would serve to indicate those industrial markets in which they might be utilized as raw materials. The possibility of increasing the tar-acid yield from hydrogenation of coal can be estimated from a study of the degradation of the primary asphaltic products to learn whether the molecular weight could be reduced without the elimination of oxygen as water.

The tar-acid fraction of the n-hexane-soluble portion (oil) of the liquid product obtained by mild hydrogenation of Pittsburgh-bed (Bruceton) coal (to produce fuel oil as the major product) was isolated by extraction of a benzene solution of the oil with alcoholic sodium hydroxide. The yield of tar acids was 9.4 percent by weight of the n-hexane-soluble oil, 5.2 percent of the total oil produced in the hydrogenation, or 4.0 percent based on moisture- and ash-free coal. The tar acids were subjected to distillation, and 136 fractions were collected. On the basis of refractive indexes and boiling points, these were combined into 70 fractions. Chemical and physical investigation of selected fractions resulted in the isolation and identification, either as pure compounds or derivatives, of 16 individual phenols.

The quantities in which the lower-boiling (C_6-C_8) phenols occurred were determined by infrared spectrophotometry and are shown in table 19. The fractions in which they are found are shown in table 20.

In the lower-boiling fractions, phenol and o-cresol were isolated as pure compounds and m- and p-cresol as m- and p-methylphenoxyacetic acids. Four isomeric xylenols were found. 3,5-xylenol and 2,5-xylenol were isolated as pure compounds. 2,4-xylenol was identified through its N-(2-fluorenyl)-carbamate; 3,4-xylenol was not detected by chemical methods, but was shown by infrared spectroscopy to be present in small quantities. Of the ethyl-phenols, only one, m-ethylphenol, was identified by chemical means; 0- and p-ethylphenols were shown to be present by infrared spectroscopy. The distribution of the tar acids in the phenol-through-oxylenol range is shown in table 21.

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[77] Golumbic, N., Some Chemicals from Synthetic Liquid Fuels Processes: Bureau of Mines Rept. of Investigation 4467, 1949, 58 pp.

TABLE 19. - Yields of tar acids from mild hydrogenation of Bruceton coal (to produce a fuel oil as the major product)

Compounds	Percent of hexane soluble oil	Percent of total oil	Pounds per ton of total oil	Pounds per tons 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	.24	.14	2.8	2.2
3,4-xylenol	.05	.03	0.6	0.5
O-ethylphenol	.03	.02	0.4	0.3
m-ethylphenol	.42	.23	4.6	3.6
p-ethylphenol	.09	.05	1.0	0.8
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
Total	3.20	1.77	35.4	27.6

[1] Dry, ash-free coal.

TABLE 20. - Fractions in which identified phenols were found

Fraction	B.P., °C.	Press., mm. Hg	Compounds	Identification
4-7	97-99	40	Phenol	Pure and as phenyl N-phenylcarbamate.
8-21	99-102	40	o-cresol	Cineole derivative.
			Phenol	As tribromophenol.
22-24	100-104	40	o-cresol	Pure and as N-phenylcarbamate derivative.
34-40	114-115	40	m-cresol	As tribromo m-cresol.
			p-cresol	As aryloxyacetic acid derivative.
44-47	116-120	40	2,5-xylenol	Pure and as N-phenolcarbamate derivative.
			2,4-xylenol	As N-(2-fluorenyl) carbamate derivative.
48-51	121-125	40	2,4-xylenol	p-Nitrobenzylether derivative.
			2,3-xylenol (?)	Aryloxyacetic acid derivative (but not by infrared).
			Mesitol (?)	Methoxytrimesic acid - trimethyl ester (but not by infrared).
56-61	129-130	40	M-ethylphenol	Aryloxyacetic acid derivative.
			o-ethylphenol	Infrared spectrometry.
63-65	130-131	40	p-ethylphenol	Infrared spectrometry.
			3,5-xylenol	Pure as N-phenylcarbamate derivative.

TABLE 20. - Fractions in which identified phenols were found (Cont'd.)

Fraction	B.P., °C.	Press., mm. Hg	Compounds	Identification
77-82	141-145	40	3-methyl-5-ethylphenol	As benzoate, n-phenylcarbamate and aryloxyacetic acid derivatives, infrared spectrometry.
85	149-151	40	4-indanol	Pure and ultraviolet analysis.
99	156-159	40	5-indanol	Pure and ultraviolet analysis.
105-107	161-164	40	Symmetrical C_{10} phenols and methyl homologues of 5-indanols.	Spectroscopic data and chemical derivatives.
117-118	165-168	30	o-phenylphenol	Pure and as aryloxyacetic acid derivative.
135	197-203	30	p-phenylphenol	Pure and ultraviolet analysis.

TABLE 21. - Distribution of the tar acid in phenol-through-oxylenol range

Compounds	Grams in tar acid fractions	Percent of total tar acids	Percent of total C_6-C_8 fractions
Phenol	111.5	2.6	9.3
o-cresol	169.9	3.9	14.1
m-cresol	255.7	5.9	21.3
p-cresol	115.3	2.7	9.6
2,4-xylenol	103.2	2.4	8.6
2,5-xylenol	63.7	1.5	5.3
3,5-xylenol	115.9	2.7	9.6
3,4-xylenol	20.6	0.5	1.7
o-ethylphenol	14.9	0.3	1.2
m-ethylphenol	188.0	4.4	15.6
p-ethylphenol	43.8	1.0	3.6
	1,202.5	27.9	99.9

A new analysis for hydroxyl oxygen in coal-hydrogenation oils was developed, which involves reaction of the oil in dry pyridine with Grignard reagents; hydroxylic compounds are known to enter quantitatively into this reaction with the formation of stoichiometric amounts of methane. Previous analyses were based on an extraction of the oil with aqueous or alcoholic alkali. Aqueous alkali is not suitable extraction agent because of the limited solubility of high-boiling phenols in such a medium. The use of alcoholic alkali improves the extractibility but involves the troublesome question of distribution of neutral oil in the system. Compounds other than the hydroxylic type, containing active hydrogen atoms, would react with Grignard reagents and interfere with the determination of oxygen. The principal source of such an error is primary amines, but investigation has shown that the heavier oils obtained from coal hydrogenation contain little amino nitrogen; most of the nitrogen present is cyclic in nature, as indicated by the fact that it is eliminated only slowly from coal. This method cannot, of course, discriminate between phenolic and aliphatic hydroxyl groups, but treatment with Grignard reagents of a benzene extract of an alkali extract of the oil showed that approximately 29 percent of the total oxygen in the oil was phenolic in nature.

Ultraviolet spectrometry continues to be of great importance in the aromatic cyclodehydrogenation studies[78] [79] that are being made to assist in the identification of polynuclear hydrocarbons present in coal hydrogenation oils and to provide an understanding of their mode of formation.

The preparation of isomeric 1-aminofluorene was reported.[80] The synthesis consisted essentially of the oxidation of fluoranthane to fluorenone-1-carboxylic acid, reduction of the latter to fluorene-1-carboxylic acid, and replacement of the carboxyl group by an Amino group.

A new general synthesis of fluoranthene and its derivatives was reported.[81] The anhydride resulting from the condensation of fluorene and maleic anhydride was cyclized to 1-carboxy-3-keto-1,2,3,10 b-tetrahydro fluoranthene, which was then reduced and dehydrogenerated to fluoranthene-1-carboxylic acid. The carboxyl group was esterified, and Curtius degradation of the ester gave 1-aminofluoranthene.

Installation of batch distillation equipment has been completed. Batches of 50 to 500 gallons of oil can be distilled in this equipment to provide large samples of gasoline, Diesel oil, or byproduct tar acids for practical tests and for precision separations to be conducted by the distillation group of the organic chemistry section. The latter has been engaged in development of standards for vacuum distillation and in design and erection of a number of precision stills. A photograph of the pilot-plant scale equipment is shown in figure 35, and of a typical still assembly in figure 36.

LIQUEFACTION OF COAL BY HYDROGENATION OF CARBON MONOXIDE: RESEARCH AND DEVELOPMENT

The process for the production of liquid fuels by the hydrogenation of carbon monoxide in the internally cooled (by oil circulation through a bed of catalyst granules) converter has been greatly improved, and relatively cheap, durable catalysts have been found for the process. Since 1942, industrial activity in the United States has centered about the application of the fluidized catalyst technique to the synthesis. The Bureau of Mines, however, has continued the development of other types of Fischer-Tropsch processes, and a second process is now in the pilot-plant stage of development. In this process, the finely powdered catalyst is suspended in a high-boiling oil, and the synthesis gas is bubbled through the suspension. Rate measurements in laboratory reactors and X-ray and magnetic studies of catalysts have resulted in a clearer understanding of the nature of the catalytic processes involved.

78/ Woolfolk, E. O., and Orchin, M., Preparation of 2,4,7-Trinitro fluorenone: Org. Syn., vol. 28, 1948, p. 91.

79/ Orchin, M., Woolfolk, E. O., and Reggel, L., Aromatic Cyclohydrogenation VIII. Experiments with 2-Benzoyl - 5,6,7,8-tetrahydronapthalene; Jour. Am. Chem. Soc., vol. 71, 1949, p. 1126.

80/ Bergman, E., and Orchin, Milton, Synthesis of 1-Aminofluorene: Jour. Am. Chem. Soc., vol. 71, 1949, pp. 1111-1112.

81/ Bergman, E., and Orchin, Milton, Synthesis of Fluoranthene and Its Derivatives: Jour. Am. Chem. Soc., vol. 71, 1949, pp. 1917-1918.

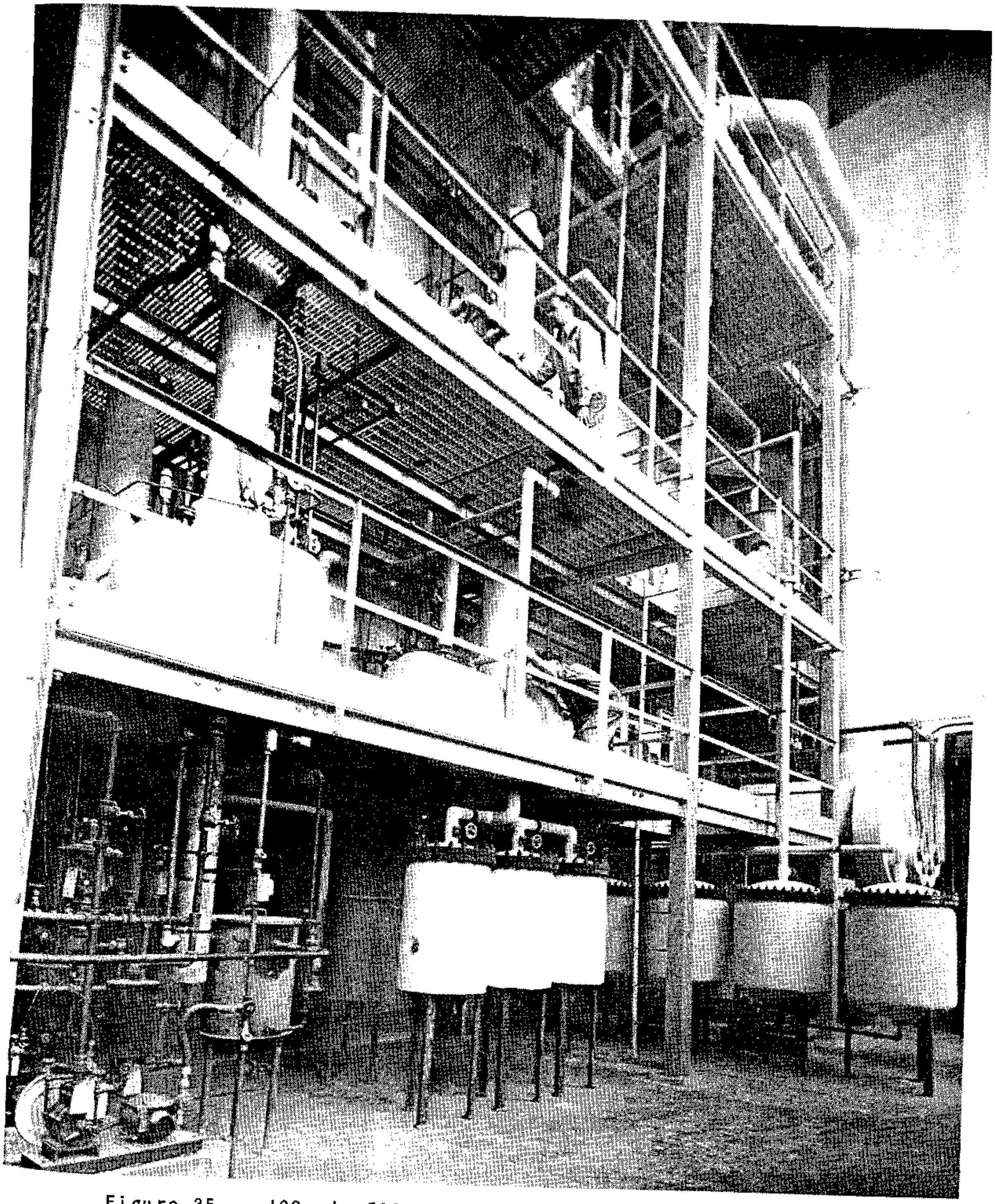

Figure 35. - 100- to 500-gallon batch-distillation equipment.

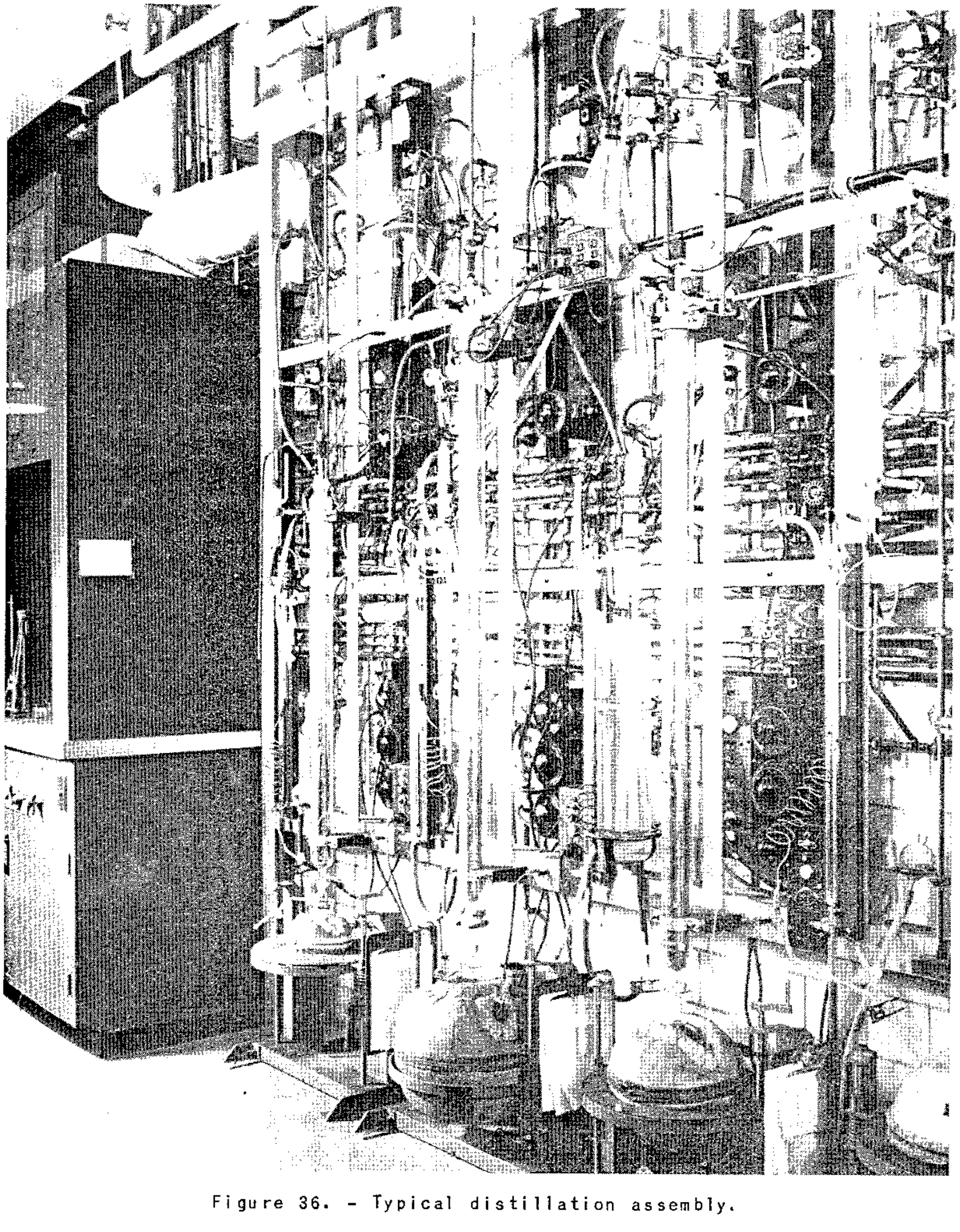

Figure 36. - Typical distillation assembly.

Cost estimates on Fisher-Tropsch processes, starting with coal as the source of carbon, show that a very large fraction of the cost of production of liquid fuels is the cost of synthesis-gas production. A study of this phase of the process, therefore, is of obvious importance.

The dependence of the Fischer-Tropsch synthesis upon space velocity of synthesis gas, temperature, pressure, and synthesis-gas composition was reviewed.[82] The effects of these operating variables upon the over-all synthesis rate and upon the molecular weight distribution and degree of unsaturation of synthesis products were interpreted in terms of a simplified, unitary picture of the elementary processes occurring during synthesis. Recent work on the role of metal carbides as intermediates in the synthesis was considered. With cobalt catalysts, bulk carbide seems to be neither an intermediate nor a catalyst for the synthesis.

The research and development program for synthesis of liquid fuels by hydrogenation of carbon monoxide is outlined as follows:

A. Reaction Mechanism Studies.
   1. Surface Areas and Densities of Iron Catalysts.
   2. Effect of Carriers and Promoters in Cobalt Catalysts and Role of Bulk Metal Carbides in the Synthesis.
   3. Effect of Chloride Ion upon the Activity of Iron Catalysts.
B. Catalyst Activity and Durability.
C. Study of Fundamental Properties of Fixed and Fluidized Beds.
   1. Heat Transfer Through Fluidized Beds.
   2. Flow Through Fixed Granular Beds.
   3. Flow Through Fluidized Beds.
D. Process Development, Bench Scale.
E. Process Development, Pilot-plant Operations.
F. Separation and Identification of Products of Hydrogenation of Carbon Monoxide.

Reaction Mechanism Studies

Surface Areas and Densities of Iron Catalysts

Determination of surface area and mercury and helium densities of fused iron catalysts showed that, during reduction, the external volume of the catalyst particle

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[82] Weller, Sol , Effect of Operating Variables on the Fischer-Tropsch Synthesis: Bureau of Mines Rept. of Investigation 4405, 1949, 8 pp.

remains the same, and pores are developed by removing oxygen from the interior of the grain. The average pore diameters (330 to 350Å) remain very nearly constant throughout the reduction and are not widely different from those found in reduced cobalt catalysts (327 to 672Å). Surface areas were found to vary almost linearly with extent of reduction. At 90 to 100 percent reduction, however, it appears that some sintering occurs, as the surface area does not increase as much as the pore volume.

Similar studies with precipitated iron catalysts suggest an explanation for the greater activity of precipitated catalysts as compared to fused catalysts. The surface of the precipitated catalysts may be more accessible to the reacting gases owing to the presence of pores with diameters about three times as large as those found in fused catalysts. Similarly, reduced cemented catalysts, having pores about 1,400Å in diameter, are more active than reduced fused catalysts (pore diameter, 300Å).

Effect of Carriers and Promoters in Cobalt Catalysts and Role of Bulk Metal Carbides in the Synthesis

A number of commercially available American kieselguhrs were studied in connection with promoted cobalt catalysts.[83] Acid-extracted natural kieselguhrs produced catalysts of the highest activity. The density of the catalyst varied directly with the density of the kieselguhr, and the distribution of products changed with density of the catalysts, the denser catalysts forming a greater percentage of light hydrocarbons and carbon dioxide. Kieselguhr as a carrier was primarily effective in preventing a decrease in bulk volume of the catalyst on reduction. The promoters were found to prevent excessive decreases in surface area on reduction, and carbon monoxide chemisorption studies showed that an appreciable fraction of the surface was occupied by promoter.[84] Decrease in the accessibility of the surface of these catalysts, either by deposition of excessive quantities of wax or by reduction of average pore diameter by pelleting, caused an increase in the fraction of light hydrocarbons and, in some cases, a decrease in activity.[85]

X-ray diffraction patterns of cobalt and iron carbides combined with the magneto-chemical constants and earlier determinations of such patterns and constants for the iron oxide phases[86] have provided the essential elements for analysis of Fischer-Tropsch catalysts by physical methods. Although little or no metal carbide

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[83] Anderson, R. B., Krieg, A., Seligman, B., and Tarn, W. H.: Fischer-Tropsch Cobalt Catalysts. Influence of Type of Kieselguhr: Ind. Eng. Chem., vol. 40, 1948, pp. 2347-2351.

[84] Anderson, R. B., Hall, W. K., and Hofer, L. J. E.: Studies of the Fischer-Tropsch Synthesis. IV. Properties of Reduced Cobalt Catalysts: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 2465-2472.

[85] Anderson, R. B., Hall, W. K., Krieg, A., and Seligman, B., Studies of the Fischer-Tropsch Synthesis, V. Activities and Surface Areas of Reduced and Carburized Cobalt Catalysts: Jour. Am. Chem. Soc., vol. 71, 1949, pp. 183-188.

[86] 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. Part I. Review of Literature; Bureau of Mines Research on Effect of Catalyst Preparation, Reduction, and Induction Procedures on Activity; Correlation of Physical Properties of the Catalysts with Their Activity: Bureau of Mines Tech. Paper 709, 1948, 213 pp.

is formed when the synthesis is conducted on cobalt catalysts[87] and extensive precarbiding greatly reduces the activity of these catalysts, the reverse is true for iron catalysts. Precarbiding of iron catalysts prepared by precipitation from solutions of iron and promoter metal nitrates yields very active catalysts. Where no precarbiding is done, iron catalysts form large amounts of iron carbide during the first few weeks of operation. Thermodynamically, however, it is impossible to account for more than about 0.005 percent of the total olefins in the product of the synthesis from hydrogen on iron carbide, and no appreciable amounts of saturated hydrocarbons larger than hexane are possible. It is probable, therefore, that the beneficial action of iron carbides is confined to that of a promoter.

The relationship between the carbides of formula Fe_2C, which were reported in thermomagnetic studies of Pichler and Merkel, and those reported in X-ray diffraction studies of various workers such as Hägg, Jack, and Halle and Herbst was established. The existence of two carbides of iron with the formula Fe_2C was confirmed. One carbide is identical with that described by Hägg; its Curie point is 247° C. The other carbide is identical with the hexagonal close-packed described by Halle and Herbst; its Curie point is 380° C. The latter carbide is converted above 300° C. to the Hägg carbide, which in turn is decomposed at 550° C. to cementite, Fe_3C, and carbon.[88]

After reduction and carburization of precipitated iron catalyst, X-ray diffraction analysis showed the presence of hexagonal, close-packed Fe_2C. The mode of transition from Fe_2C-Hägg to cementite, Fe_3C, was studied by following the course of the magnetic curves between the Curie points of the carbides; the transition was found to be discontinuous, which means that precipitation starts with the formation of nuclei of the new crystal habit, followed by their growth at the expense of the existing structure.

The change in the composition of a fused iron catalyst was studied during its use in the medium-pressure Fischer-Tropsch synthesis. X-ray diffraction and thermomagnetic analyses showed that Hägg carbide (Fe_2C) was formed very rapidly during the beginning of the experiment; a maximum amount had been formed sometime during the first three days of operation, after which it decreased linearly with time. No carbides other than Fe_2C-Hägg were identified. Similar examination of used iron catalysts after catalyst-testing studies showed that, of the three known ferromagnetic iron carbides, the hexagonal, close-packed Fe_2C is rarely formed with fused catalyst under the usual synthesis conditions, and that cementite, Fe_3C, does not appear to be formed during the synthesis except by over-heating and simultaneous decomposition of the other forms of carbide.

Because of some uncertainty in the conclusions from the work with radioactive carbon as a tracer, kinetic and isotopic tracer studies with nonradioactive C^{13} isotope were begun. An apparatus was constructed for this work in which the reaction rate is measured in terms of volume changes by means of a gas burette as the gases are circulated over the catalyst samples at constant temperature and pressure. The first study involved the rate of exchange of carbon between carbon monoxide and a fully carbided cobalt catalyst. As this catalyst contained a small amount of

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[87] Hofer, L. J. E., Cohn, E. M., and Peebles, W. C., Isothermal Decomposition of the Carbide in a Carburized Cobalt Fischer-Tropsch Catalyst: Phys. and Colloid Chem., vol. 53, 1949, pp. 661-669.

[88] Hofer, L. J. E., Cohn, E. M., and Peebles, W. C., The Modifications of the Carbide Fe_2C; Their Properties and Identifications: Jour. Am. Chem. Soc., vol. 71, 1949, pp. 189-195.

graphite as a pelleting lubricant, the rate of exchange between carbon monoxide and graphite was investigated as a preliminary step. Enriched carbon monoxide, containing 3.4 percent $C^{13}O$ and prepared as described in last year's report, was circulated over the graphite at 200° C. and 306 mm. mercury pressure for 17.5 hours. The enrichment of the carbon monoxide before and after circulation was determined in the mass spectrometer. No loss in enrichment was detected. The exchange between carbon monoxide and graphite is therefore of no significance in rate studies on this catalyst.

One of the worst features of Fischer-Tropsch catalysts is their tendency to form relatively inert free carbon during the synthesis. This carbon plugs up the reaction vessel in fixed-bed converters; in fluidized-bed converters it exerts a disintegrating effect on the catalyst particles, converting them into a fine dust that cannot be retained in the converter. In addition, it is thought that carbon deposition exerts a specific poisoning action on the Fischer-Tropsch reaction. Carbon may very probably be formed by way of carbide, as follows:

$$2CO + xM \;\ldots\ldots\ldots\ldots\ldots\; M_xC + CO_2 \qquad (1)$$

$$M_xC \;\ldots\ldots\ldots\ldots\ldots\ldots\; xM + C \text{ (free)} \qquad (2)$$

This theory is supported by the fact that only those metals that form metastable carbides are known to form free carbon from carbon monoxide. Reaction (2) is simply the thermal decomposition of the carbide involved.

As subject for a study to determine the nature of this decomposition reaction, nickel carbide was chosen, because (1) it could be prepared in a well-crystallized and pure form, (2) its crystal structure is well known, and (3) it is, like carburized cobalt catalyst, nonferromagnetic. Therefore, the thermal stability of the carbide (weight ratio, C:Ni = 0.0722:1) could be studied magnetically by the same method used previously for Co_2C, and the appearance of ferromagnetism could be ascribed to the formation of ferromagnetic nickel metal, a measure of the process of the decomposition. Results of the study showed that the apparent energy of activation (67 kg. cal./mol) for the decomposition of nickel carbide is of the same order of magnitude as that found for the decomposition of a carburized cobalt catalyst (54.3 kg. cal./mol). The decomposition of nickel carbide was found to be preceded by an induction period that decreased with increasing temperature. This induction period indicates that the reaction requires the presence of nuclei that are difficult to form, but which, when formed, allow the reaction to proceed at a relatively rapid rate. Inhibiting the formation of these nuclei by various additives would, theoretically, delay the thermal decomposition.

Effect of Chloride Ion upon the Activity of Iron Catalysts

Early in the development of the Fischer-Tropsch catalysts, it was found that active catalysts could not be prepared from ferric chloride. However, precipitated catalyst of composition $75Fe^{+2}$-$25Fe^{+3}$-20Cu-0.$2K_2CO_3$, which was prepared from ferrous, ferric, and cupric chlorides according to the procedure of Pichler, produced an average yield of 88.3 g. of C_5+ hydrocarbons per cubic meter of water gas when tested for 46 days at 7 atmospheres pressure and an average temperature of 229° C. Tests made with several preparations in which the constituents of this catalyst were varied showed that the ferrous iron was the significant constituent.