Synthesis of Liquid Fuels by Hydrogenation of Coal

Experiments in Small Autoclaves

Data obtained in the absence of high-pressure hydrogen show that solvents for bituminous coal may be grouped into three classes: The very good solvents 1, 2, 3, 4-tetrahydro-5-hydroxynaphthalene and 0-cyclohexylphenol; the moderately effective solvent tetralin; and the less effective solvents dicyclohexyl, 2-methoxy-1-cyclohexylbenzene, diphenyl, naphthalene, cresol, and o-phenylphenol. This classification of solvents on the basis of their effectiveness can be correlated with the chemical structure of the solvents. The least effective group of solvents can dissolve 20 to 30 percent of the coal at 400° C. Apparently the only requirement for this action is that the solvent be a high-boiling aromatic compound or a hydroaromatic compound that is only slowly dehydrogenated under these conditions. If the solvent can function as a good hydrogen donor, its effectiveness is enhanced. Tetralin is easily dehydrogenated and accordingly gives moderately good liquefaction results. If, in addition to a hydroaromatic ring, a solvent possesses an aromatic hydroxyl group, this solvent is an extremely effective vehicle for liquefying coal. Such solvents are o-cyclohexylphenol and 1, 2, 3, 4-tetrahydro-5-hydroxynaphthalene.

In the group of less-effective solvents, the hydroaromatic compounds are generally superior to the completely aromatic compounds. The effectiveness of tetralin and the other hydroaromatic solvents is almost certainly due to their ability to act as hydrogen donors to the coal substance. In pure compound studies, it has been shown[70] that tetralin can readily hydrogenate anthracene. It was of considerable interest in the present instance to learn the extent of the hydrogen transfer from o-cyclohexylphenol to coal. At the conclusion of one solvation experiment, the cyclohexylphenol-phenylphenol fraction was separated from the reaction mixture by distillation at atmospheric pressure and the ultraviolet absorption spectrum of this mixture determined. The spectra showed the conversion of 9 percent o-cyclohexylphenol to o-phenylphenol which corresponded to a hydrogen consumption of 1.4 percent by the dry, ash-free coal. This small consumption of hydrogen was very effective in producing liquefaction of the coal.

The effectiveness of a small quantity of hydrogen available from a hydrogen donor like tetralin is illustrated by another series of solvation experiments. In this group of experiments the solvent consisted of a mixture of tetralin and cresol in varying proportions. In each experiment, 160 grams of solvent mixture was heated with 40 grams of coal for 0.5 hour at 400° C. The results are shown in figure 49. These results show that the addition of small quantities of cresol to tetralin or the addition of small quantities of tetralin to cresol results in higher liquefaction than that obtained with the pure solvent alone. The addition of a small amount of tetralin to cresol appears to have a particularly great effect. This effect can be ascribed to the influence of the small but effective quantity of hydrogen furnished by the tetralin.

70/ Orchin, M., Hydrogenation of Anthracene by Tetralin: Jour. Am. Chem. Soc., vol. 66, 1944, pp. 535-538.

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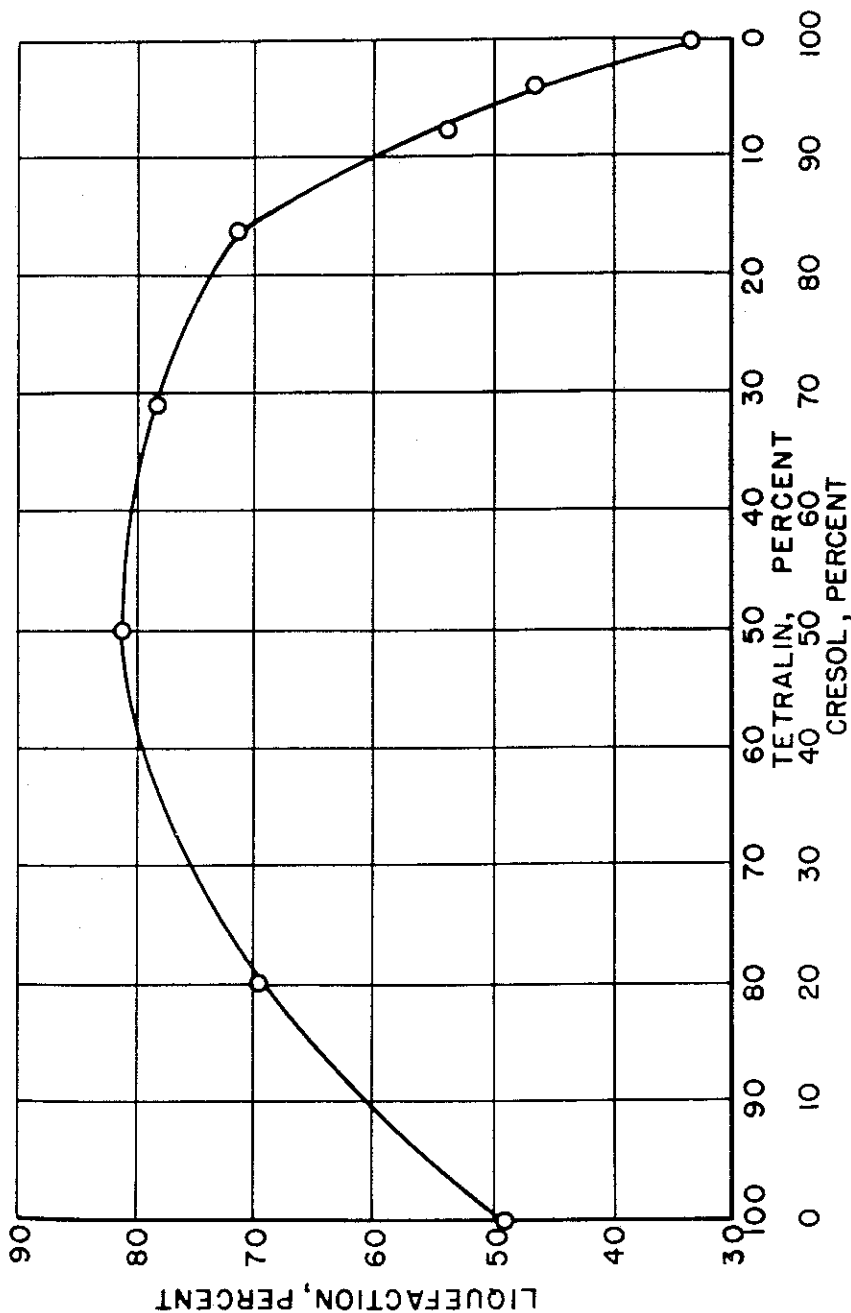dition
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Figure 49. – Solvation experiments with various proportions of tetralin and cresol.

The effectiveness of a small quantity of hydrogen in producing coal liquefaction is probably due to the hydrogenolysis of some peculiarly susceptible linkages in the coal structure. Thermal treatment alone does not sever these bonds to produce a liquid product; but if the coal is made to consume about 1 to 2 percent hydrogen, a completely liquid product can be obtained. The hydrogenolyzed bonds are very probably carbon-to-oxygen bonds.

The effect of an hydroxyl group in the solvent is indeed striking. 1, 2, 3, 4-tetrahydronaphthalene gives about 50 percent liquefaction; 1, 2, 3, 4-tetrahydro-5-hydroxynaphthalene gives 85 percent liquefaction. The methyl ether of cyclohexylphenol (o-methoxycyclohexylbenzene) gives 29 percent liquefaction; o-cyclohexylphenol gives 82 percent liquefaction. The effectiveness of the hydroxyl group is probably related to its hydrogen bonding properties.

The effect of concentration of the hydroxylated solvent in a mixture used for the solvation of coal is shown in table 31. In these experiments, a mixture of various concentrations of o-cyclohexylphenol in the methyl ether of o-cyclohexylphenol was used as the vehicle. The results show that a large excess of the hydroxylated solvent must be present to obtain good liquefaction of coal.

TABLE 31. - Solvation experiments at 400° C. (0.5 hour), using various concentrations of 0-cyclohexylphenol (R-OH) in 2-methoxy-1-cyclohexylbenzene (R-O-CH$_3$)

Vehicle	Liquefaction, percent
100 percent R-OH	81.6
38 percent R-OH; 62 percent R-OCH$_3$	50.2
8 percent R-OH; 92 percent R-OCH$_3$	32.6
100 percent R-OCH$_3$	30.2

The solutions of coal in cyclohexylphenol are quite stable. In one experiment such a solution was kept in air at 45° for 19 days. During this time, virtually no material precipitated. The word "solution" is used in the sense that no material can be separated from the solutions by ordinary centrifugation or filtration. Microscopic examination of these solutions at 400 magnification showed them to be substantially free of solid particles. It is conceivable that the "solutions" are colloidal dispersions.[71]

In the presence of high-pressure hydrogen, the degree of liquefaction obtained with hydroaromatic compounds was substantially the same as that with the corresponding aromatic compound. Under solvation conditions, however, the hydroaromatic compound in each instance gave superior results. It is apparent that, under solvation conditions, a hydrogen-donor vehicle is superior to a completely aromatic vehicle, while, under hydrogenation

[71] Kreulen, D. J. W., Fuel: Vol. 24, 1946, p. 99. This is an article of special interest in connection with the colloidal nature of coal.

conditions, the high-pressure hydrogen serves as the principal source of hydrogen, and the hydroaromatic feature of structure of the vehicle is no longer essential for good liquefaction results. The higher consumption of hydrogen observed with the aromatic partner of each pair was due to hydrogenation of the aromatic vehicle. That the hydroaromatic feature of structure is without significance in hydrogenation experiments is also shown by a comparison of results with cresol under solvation and hydrogenation conditions. The presence of high-pressure hydrogen increased the liquefaction from 32.1 percent to 91.7.

Although under hydrogenation conditions it does not appear to make much difference whether an aromatic, a hydroaromatic, or a naphthenic compound is used, considerable advantage is to be gained from using material as a vehicle that contains an aromatic hydroxyl group.

Detailed data have been obtained on the efficiency of zinc-antimony and tin-zinc-antimony mixtures as catalysts in the conversion of bituminous coal to heavy oil. In the presence of tin and ammonium chloride, which is the catalyst usually employed for liquefaction of bituminous coal, the production of benzene-soluble material is quite rapid, but the conversion of this material to a petroleum ether-soluble oil is a slow reaction. This is illustrated by figure 50 from which it is seen that the rate of disappearance of asphaltic material (benzene-soluble, petroleum ether-insoluble) is slow at temperatures below about 450° C. The efficiency of new catalysts in accelerating conversion of asphaltic materials to petroleum ether-soluble oil is best-studied at temperatures below 450° C. In figure 51, the efficiencies at 415° C. of 1 percent tin metal, 1 percent zinc-antimony alloy, and 0.5 percent tin metal plus 0.5 percent of zinc-antimony alloy are shown. It is apparent that tin is a good liquefaction catalyst but a relatively poor one in accelerating asphalt conversion, whereas the reverse is true for zinc-antimony alloy, which is a poor liquefaction catalyst but which greatly accelerates asphalt conversion. The ternary catalyst containing tin, and zinc-antimony alloy is very efficient for both liquefaction and asphalt conversion.

Separation and Identification of Constituents of Synthetic Liquid Fuels

The steps in the separation and identification of synthetic liquid-fuel components are: Primary distillation; separation of distillation fractions into types of compounds by solvent extraction or by adsorption on alumina or silica gel; precision distillation; analysis of lower-boiling constituents by spectrometric methods; identification of higher-boiling constituents by measurements of density; refractive index; and preparation of pure derivatives of known melting point. The laboratories in which these procedures are conducted are the precision distillation laboratory shown in figure 52, the spectrometric laboratory, figure 53; and the organic laboratory, figure 54.

The limitations of atmospheric pressure distillation were clearly recognized as a result of work on the characterization of light oil from coal hydrogenation.[72]

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[72] Kaplan, E. H., Storch, H. H., and Orchin, M., Hydrogenation and Liquefaction of Coal. Part V. Characterization of Light Oil: Bureau of Mines Tech. Paper 690, 1946, 18 pp.
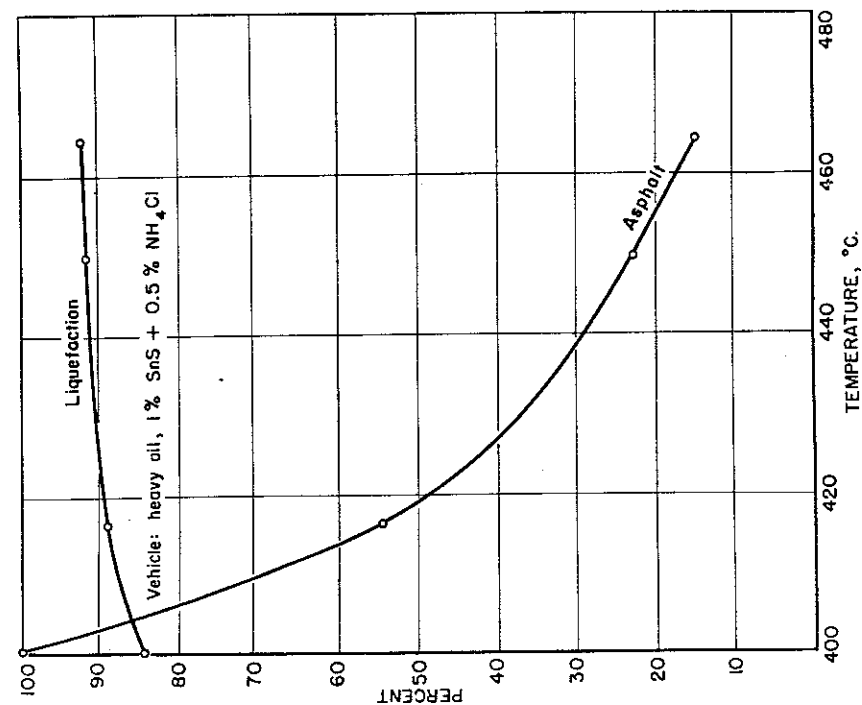
Liquefaction (3)
Liquefaction (1)
Liquefaction (2)

In presence of   1% Sn (1)(4)
     "   "   1% Zn-Sb (2)(5)
     "   " $\frac{1}{2}$% Sn + $\frac{1}{2}$% Zn-Sb (3)(6)

Asphalt (5)
Asphalt (4)
Asphalt(6)

TIME, MINUTES

PERCENT

Figure 51. – Liquefaction of coal and asphalt formation at 415° C.

Liquefaction

Vehicle: heavy oil, 1% SnS + 0.5 % NH_4Cl

Asphalt

TEMPERATURE, °C.

PERCENT

Figure 50. – Effect of temperature on liquefaction and asphalt formation.
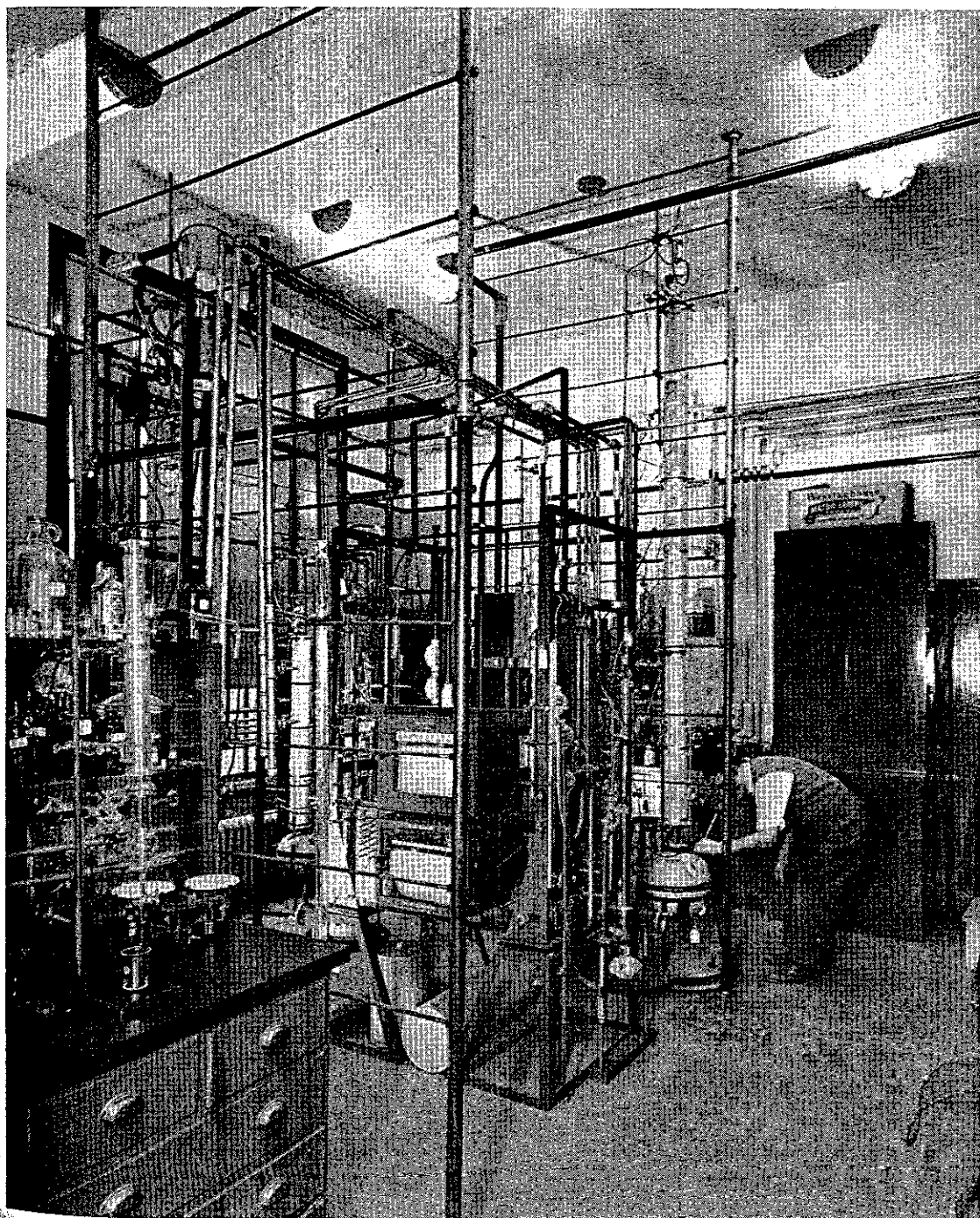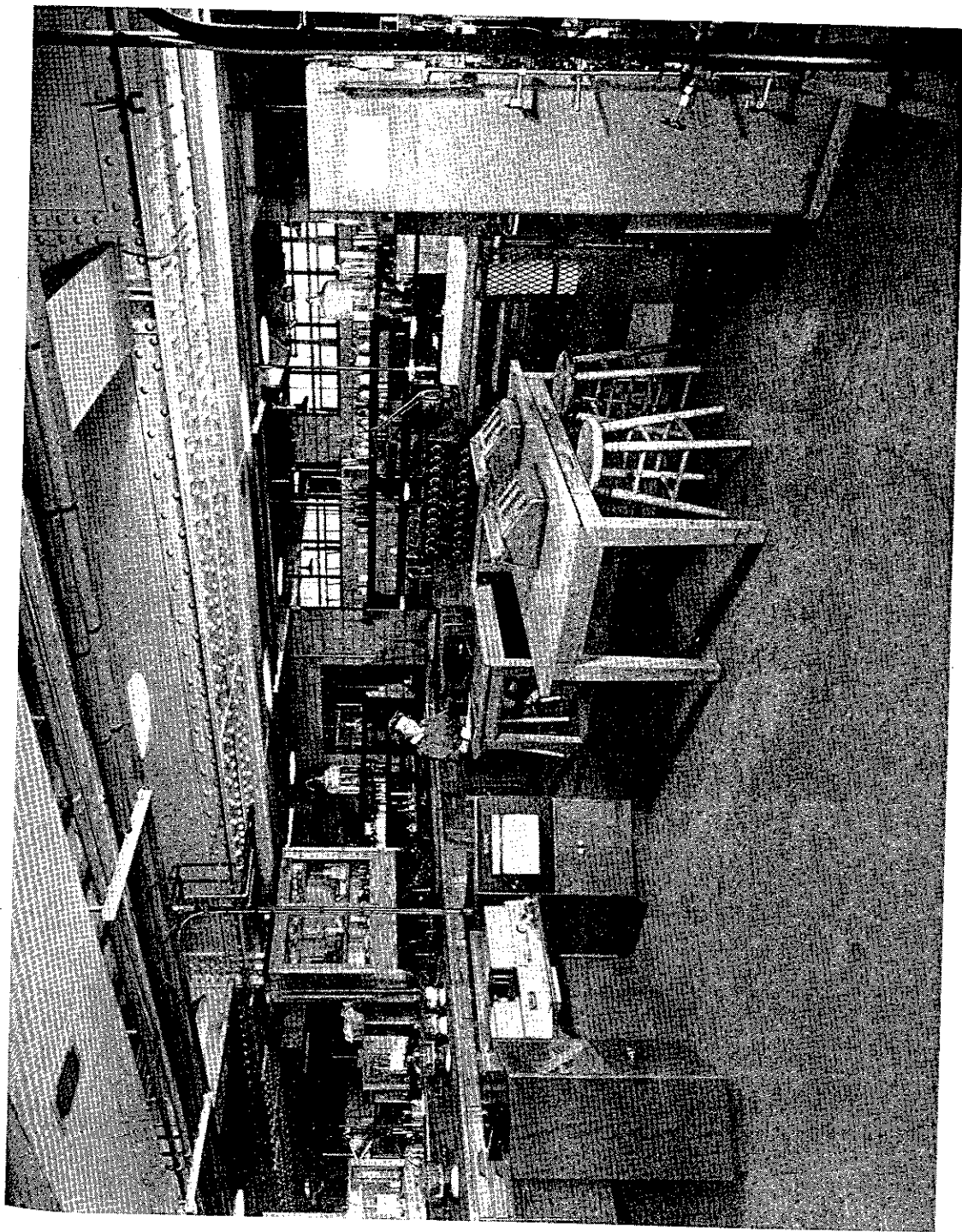
Figure 52. - Precision distillation laboratory.

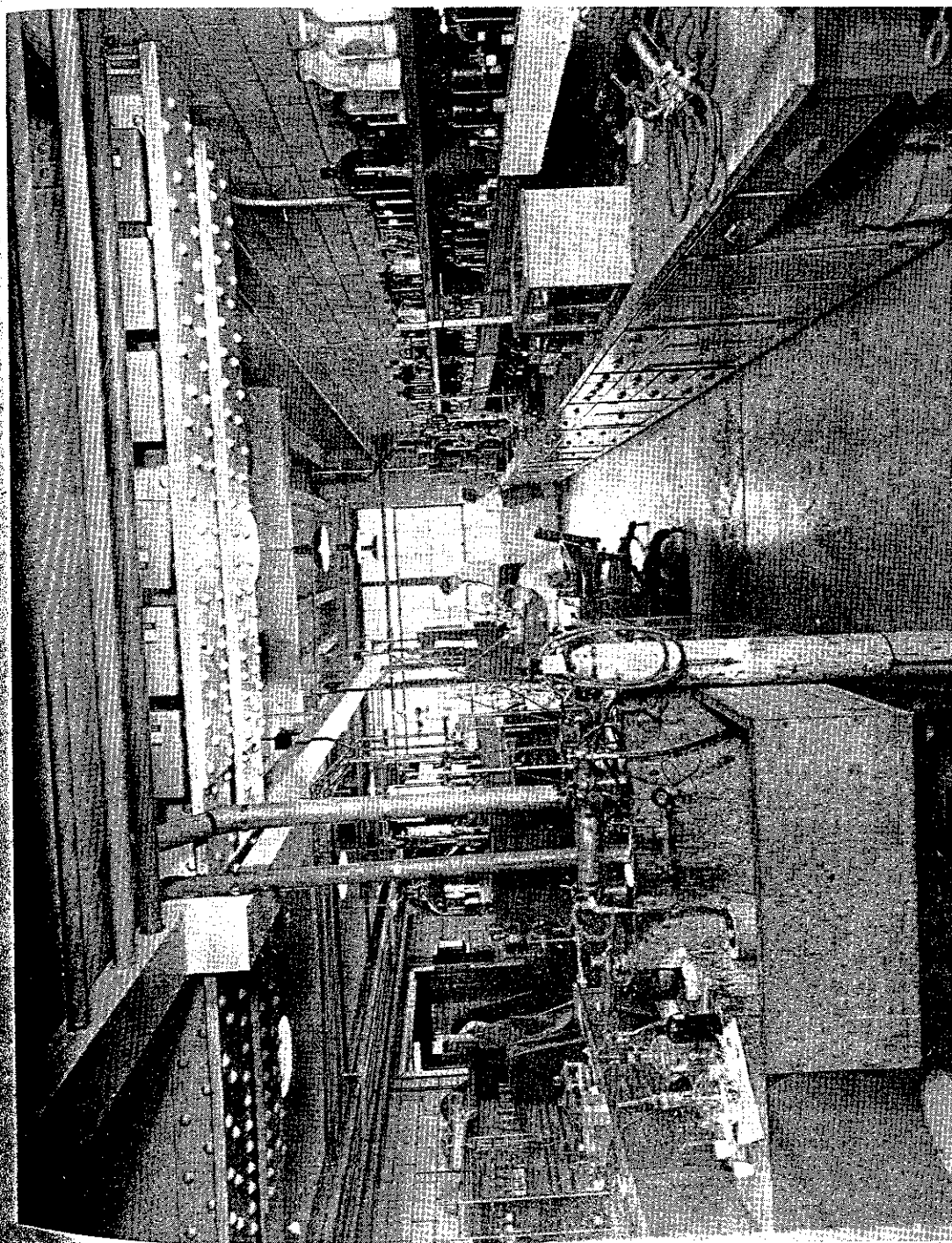Figure 53. - Spectrometric laboratory.

Figure 54. - Organic chemistry laboratory.

For the characterization of high-boiling oils from both the Fischer-Tropsch and the coal-hydrogenation processes, precise vacuum distillation is essential. To establish satisfactory standards for vacuum distillation, several pairs of compounds whose boiling point and other physical properties differ only to a small degree are being investigated. Cyclohexyl-cyclopentane plus n-dodecane constituted one pair and another was tridecane plus dicyclohexyl.[73] Because a study of the vapor pressures of the pure compounds and of mixtures showed that these two pairs were not entirely satisfactory as standards for precision vacuum distillation, further work is planned on the study of pairs consisting of hydrocarbons and the corresponding deutrocarbons.

For the identification of narrow boiling fractions containing only one type of hydrocarbon, their characteristic physical constants, namely, melting points, refractive indices, infra-red[74] and ultra-violet absorption spectra, are determined. In addition, the preparation of chemical derivatives, such as the complex compounds of aromatics with 2-4-7-trinitrofluorenone,[75] is useful for identification purposes.

Identification of compounds in coal hydrogenation oils and an understanding of the probable mode of formation has been aided by a study of aromatic cyclodehydrogenation of substituted aromatic compounds.[76,77]

Recent precision distillation and infra-red spectrometric work on Fischer-Tropsch products showed that all of the straight-chain paraffins up to those containing 20 carbon atoms were present in the distillable fraction (about 85 percent of the total product). About 10 percent of branched-chain paraffins, chiefly those with a methyl group in the 1 or 2 position, was present.

A new and very promising X-ray diffraction procedure for determining the extent of branching of Fischer-Tropsch products using not more than 1 cc. of sample is being developed. All normal aliphatic organic compounds, such as hydrocarbons, alcohols, and fatty acids in the liquid state, have molecular diameters (or "Bragg" spacings, as determined from the diffraction pattern) between 4.54 and 4.64 Ångstrom units, with the exception of the

[73] Orchin, M., and Feldman, J., The Isomerization of Dicyclohexyl: Jour. Am. Chem. Soc., vol. 68, December 1946, pp. 2737-2738.

[74] Friedel, R. A., McKinney, D. S., The Infra-red Absorption Spectra of Liquid and Gaseous Morpholine: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 604-607.

[75] Orchin, M., and Woolfolk, E. O., Molecular Complexes with 2-4-7-trinitrofluorenone: Jour. Am. Chem. Soc., vol. 68, 1946, pp. 1727-1729, vol. 69, 1947, pp. 1225-1227.

[76] Orchin, M., Synthesis of Fluorene and Its Derivatives: U. S. Patent 2,414,118, January 1947.

[77] Orchin, M., and Reggel, L., Aromatic Cyclodehydrogenation, Part V. A Synthesis of Fluoranthene: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 505-509.

first three or four members of the series. Branched compounds, such as 2, 2, 4-trimethylpentane, have Bragg spacings of 6.00 Angstrom units; less highly branched hydrocarbons having intermediate spacings. The Bragg spacings of straight-chain and branched chain hydrocarbons were plotted against the ratio of the numbers of carbon atoms in the branched chains to the total number of carbon atoms. The data are well-represented by a smooth curve, which will be used as a standard for determining the degree of branching of Fischer-Tropsch products which are available in only very small amounts from catalyst testing experiments.

Chemical Engineering Research, Design of Special Instruments and Equipment, and Cost Estimates on Synthetic Liquid Fuel Processes

Experiments to Provide Data for the Design of Fischer-Tropsch Pilot Plants

The data necessary for (mathematical as opposed to "intuitive") design of Fischer-Tropsch pilot plants are: A knowledge of the chemical nature of the rate-determining step in the synthesis, the temperature and pressure coefficients of the rate, complete data on the composition of the reacting system at several points along the path of the gases through the catalyst bed, the heat evolved during the synthesis, and adequate knowledge of the laws governing heat transfer in the particular process being considered. Some of these data, such as the temperature and pressure coefficients of the synthesis rate, have been obtained from recent measurements in the physical chemistry and catalyst-testing laboratories. Proof of the nature of the rate-determining step is not yet available. For the internally cooled Fischer-Tropsch converter, analysis of the composition of the reacting system at several points in the 8-foot catalyst bed is underway. Selection and improvement of the mathematical analysis procedures also are being conducted.

An analytical criterion was published[78] for the choice of individual components in systems of many constituents and relations derived[79] which form the basis for systematic calculation of the equilibrium composition of such systems as, for example, the equilibrium obtained in production of synthesis gas. These calculations are also of value in the study of the composition of the Fischer-Tropsch reacting system at intervals along the catalyst bed. Expressions were derived[80] for the temperature distribution in an adiabatic catalytic converter, as, for example, in the hot-gas recycle process.

Fuels and Lubricants Missions

Although the major portion of the work of the Fuels and Lubricants Missions to Germany was completed before the end of June 1946, five men remained

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[78] Brinkley, S. R., Jr., Note on the Conditions of Equilibrium for Systems of Many Constituents: Jour. Chem. Phys., vol. 14, 1946, pp. 563-564.
[79] Brinkley, S. R., Jr., Calculation of the Equilibrium Composition of Systems of Many Constituents: Jour. Chem. Phys., vol. 15, 1947, pp.107-110.
[80] Brinkley, S. R., Jr.,Heat Transfer Between a Fluid and a Porous Solid Generating Heat: Jour. Appl. Phys., vol. 18, 1947, pp. 582-585.

or were sent to Germany during 1947 to direct the activities of several groups of German fuels and lubricants technologists who are leading experts in their fields. These technologists have been compiling summary reports of progress in hydrogenation of coal, synthesis of carbon monoxide and hydrogen by the Fischer-Tropsch process, production of synthetic lubricants, and use of additives for improving the performance of motor fuels. Some of their reports are now being edited by the Joint Intelligence Objectives Agency. Others are now available from the Publications Board, United States Department of Commerce, and because of the broad scope of the investigations and the interest in the formation some reports have been published by the Bureau of Mines.81/82/

Samples of catalysts, fuels, and lubricants were distributed for analysis and report by the various members of the Sample Analysis Groups working under the joint sponsorship of the American Petroleum Institute and the Bureau of Mines.

The library of Foreign Synthetic Liquid Fuels information has been moved from Washington to the Bureau of Mines at Pittsburgh, Pa. Arrangements have been continued with the Library of Congress for providing copies of microfilm reels to those who cannot conveniently make use of the library facilities. There are now 1,375 separate reports prepared by 11 different groups, all relating to some phase of synthetic liquid fuels and their production.

81/ Faragher, W. F., and Horne, W. A., Interrogation of Dr. Pier and Staff I. G. Farbenindustrie A. G., Ludwigshafen and Oppau: Bureau of Mines Inf. Circ. 7376, 1946, 27 pp.
82/ Holroyd, R., Report on Investigations by Fuels and Lubricants Teams at the I. G. Farbenindustrie, A. G., Works, Ludwigshafen and Oppau: Bureau of Mines Inf. Circ. 7375, 1946, 75 pp.