produced to determine a range of synthesis-gas compositions available for experimental work. As a result of this work, it has been demonstrated that a wide range of synthesis-gas compositions can be produced on a commercial scale and that the $H_2$:CO ratio can be controlled as required.

The Bureau of Mines research program for producing synthesis gas from coal at Morgantown, W. Va., was described.[83]

## LIQUEFACTION OF COAL BY DIRECT HYDROGENATION: RESEARCH AND DEVELOPMENT

### Function of Solvents and Catalysts in Early Stages of Coal Hydrogenation

### Action of Solvents

In most of the early research on the solvent extraction of solid pyrobituminous materials, such as coal, lignite, and peat, mixtures of phenols and tetrahydronaphthalene, in which the ratio of hydrocarbon to phenols in the solvent mixture is customarily about 4:1, were used. In recent work[84] greatly improved yields of soluble materials were obtained by using as the solvent vehicle, dicyclic hydroaromatic compounds containing at least one phenolic hydroxyl group, for example, ortho- and para-cyclohexylphenol and tetrahydronaphthols. About equal parts by weight of solvent and the solid carbonizable fuel being extracted were used. The extraction was carried out using finely ground coal under pressures of 500 to 1,500 pounds per square inch. Temperatures may vary from about 250° C. to as high as 450° C., although it is preferable to operate at approximately 400° C. for typical American bituminous coals. The primary products obtained in this manner were extracts containing little or no ash which were suitable for direct use as fuels, or for use as raw materials for the production of industrial products, such as electrode carbon. Low ash extracts such as these may also be used in hydrogenation processes for the production of synthetic liquid fuels corresponding to gasoline, kerosine, and Diesel fuels from petroleum sources.

In addition to the discovery of these more efficient solvents, the possibility of efficient extraction at atmospheric pressure, with the resultant elimination of expensive, high-pressure equipment, is obviously of practical interest. Phenanthrene was observed earlier to disperse readily about 80 percent of bituminous coal. This fact served as the starting point for an investigation[85] in which determination of the chemical specificity of the solvent and the chemical nature of the extracts was undertaken. The results of these studies showed that in the extraction of bituminous coal, with solvents at their atmospheric-pressure boiling points, carbazole, phenanthridine, 5, 6-benzoquinoline, and certain homologues of these compounds (boiling range, 350° to 360° C.) were equally effective. Anthracene (b.p. 354° C.) and 1, 4-diphenylbutadiene (b.p. 350° C.), however, were shown to be decidedly inferior. Lower-boiling tricyclic compounds, fluorene and diphenylene oxide (b.p., about 300° C.), also proved to be poor solvents, but 1- and 2-naphthol (b.p. 288° and 295° C., respectively) were quite efficient. Hence, it is apparent that the effectiveness of a solvent as an extraction agent for bituminous coal is dependent upon both its molecular structure and its boiling point.

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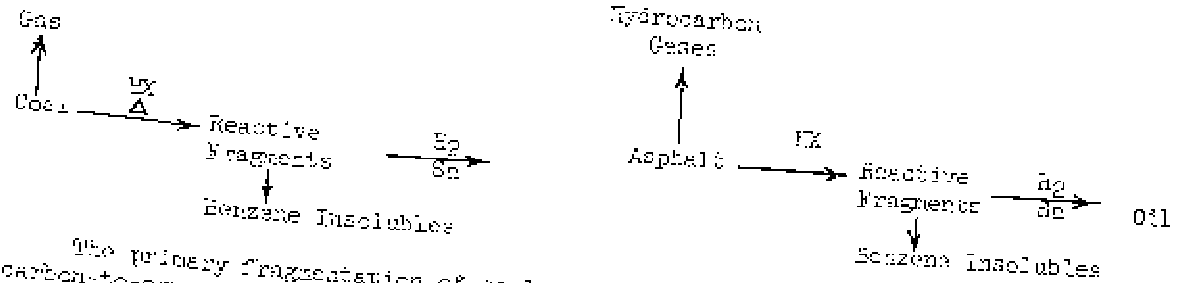
[83] Schmidt, L. D., Cooperative Work of the Federal Bureau of Mines and West Virginia University: The West Virginia Eng., vol. 12, April 1950, pp. 6-8.

[84] Orchin, M., Solvation and Depolymerization of Coal: U. S. Patent 2,476,999, July 26, 1949.

[85] Golumbic, C., Anderson, J. B., Orchin, M., and Storch, H. H., Solvent Extraction of Coal by Aromatic Compounds at Atmospheric Pressure: Bureau of Mines Rept. of Investigations 4662, 1950, 12 pp.

## Catalysts for Coal Hydrogenation; Reaction Mechanism

The primary reaction in coal liquefaction by hydrogenation is the production of reactive fragments of the coal structure, which are then stabilized either by polymerization to benzene-insoluble material or by the addition of hydrogen to form benzene-soluble material. It has been assumed that the latter reaction is catalyzed by tin.86/ The resultant benzene-soluble material is largely asphaltic. This asphalt is converted to gaseous hydrocarbons by a noncatalytic reaction and to reactive fragments by a reaction which is catalyzed by halogen-acid-producing substances (HCl, HI, $NH_4Cl$, etc.). These reactive fragments may (1) recombine to produce asphalt again, (2) polymerize still further to produce benzene-insoluble material, or (3) be stabilized by the addition of hydrogen (catalyzed by tin) to produce an oil. The following diagram indicates this scheme of reactions:



The primary fragmentation of coal, which may be associated with the splitting of carbon-to-oxygen bonds, proceeds with very little gas production. A large fraction of the oxygen in the coal is eliminated, chiefly as water. The conversion of asphaltic material to oil is probably associated with the rupture of carbon-to-carbon bonds.

The use of the proposed mechanism makes possible the interpretation of much experimental data. It can be predicted that: (1) Tin used in the absence of splitting catalyst should behave like no catalyst at all, since the splitting of asphalt to form fragments, which is assumed to precede the hydrogenation stabilization, proceeds very slowly in the absence of halogen-acid-producing substances; (2) hydrochloric acid used alone in an inert atmosphere should cause a large production of benzene-insoluble material, since stabilization of the fragments can then occur only by a disproportionation process; (3) polymerization catalysts, such as phosphoric acid, should produce especially large quantities of benzene insolubles; and (4) any substance which is both a splitting and a hydrogenation catalyst (perhaps hydriodic acid) should result in a high conversion of asphalt and a low production of benzene insolubles. These predictions were verified by experiment.

The above mechanism for the conversion of coal to oil does not explain the unique excellence of tin as a coal-hydrogenation catalyst, under a great variety of conditions of temperature and pressure and irrespective of the chemical form in which tin is used.

Experiments in batch autoclaves have shown, however, that stannous sulfide may be, thermodynamically speaking, the "least common denominator" for all forms of tin under coal-hydrogenating conditions. Calculation of the free energy changes involved

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86/ Weller, Sol, Clark, E. L., and Pelipetz, M. G., (Coal Hydrogenation Catalysts) Mechanism of Coal Hydrogenation: Ind. Eng. Chem., vol. 42, February 1950, pp. 334-336.

shows that stannic oxide can be completely converted to stannous sulfide at 700° K., provided, the hydrogen sulfide pressure is kept above 0.06 atmosphere. This condition is almost certainly met in most coal hydrogenations.

The search for a cheaper and more readily available catalyst than tin continued.[87] The only material, that was found to be as effective as tin (when catalysts are added as powdered solids) for the hydrogenation of coal, is germanium, which is even less economically desirable. Table 15 shows that at approximately 2,000 p.s.i.g. reaction pressure zinc bromide and lead bromide were markedly catalytic, resulting in liquefactions of 75 and 78 percent, respectively. It seems probable that the effect is due to the hydrogen bromide liberated under reaction conditions, which may act as a hydrogen donor as hydrogen iodide does. The study of iron catalysts for possible use in the demonstration plant has shown dried "red mud" to be promising at reaction pressures of approximately 7,500 p.s.i.g.

TABLE 15. - Hydrogenation of Bruceton bituminous coal

(In laboratory autoclaves at 450° C., 1 hour, 1,000 pounds per square inch initial $H_2$ pressure, in absence of vehicle. Pyrex glass liner used to avoid catalysis by metal walls.)

| Run No. | Catalysts | Percent of liquefaction | Asphalt per unit of liquefaction |
|---|---|---|---|
| 860... | 1 percent Sn + HI 0.55 percent $NH_4Cl$ | 87.5 | 0.21 |
| 550... | HI 0.55 percent $NH_4Cl$ | 66.6 | .39 |
| 662... | HCl 0.55 percent $NH_4Cl$ | 40.2 | .48 |
| 518... | 0.55 percent $NH_4Cl$ | 40.8 | |
| 1169.. | 1 percent Mo as $MoS_2$ + 0.5 percent $NH_4Cl$ | 49.0 | .39 |
| 1115.. | 1 percent W as $WS_2$ | 62.1 | .54 |
| 1150.. | 1 percent Ni as Ni-kieselguhr + 0.5 percent $NH_4Cl$ | 73.3 | .56 |
| 964... | 1 percent Ce as $CeO_2$ + 0.5 percent $NH_4Cl$ | 86.8 | .51 |
| 1158.. | 1 percent Ni as $NiCl_2$ | 40.0 | .28 |
| 1159.. | 1 percent Co as $CoCl_2$ | 50.6 | .53 |
| 1173.. | 1 percent Zn as $ZnCl_2$ | 44.2 | .27 |
| 1162.. | 1 percent Zn as $ZnBr_2$ | 75.2 | .22 |
| 1160.. | 1 percent Pb as $PbCl_2$ | 49.0 | .43 |
| 1161.. | 1 percent Pb as $PbBr_2$ | 76.5 | .45 |
| 1175.. | 1 percent Fe as $FeCl_2$ | 61.1 | .26 |
| 845[1] | 1 percent dried "red mud"[2] | 83.5 | .49 |
| 1181[1] | 1 percent dried "red mud"[3] | 79.0 | .46 |
| 1189[1] | 5 percent dried "red mud"[3] | 94.2 | .41 |

[1] Rock Springs coal used at 3,700 p.s.i. initial $H_2$ pressure.

[2] Obtained through the courtesy of the Aluminum Co. of America; this material is the equivalent of Bayermasse, used extensively in German coal-hydrogenation plants.

[3] Type M. obtained from Bureau of Mines, Louisiana, Mo.

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[87] Weller, Sol, Pelipetz, M. G., Friedman, Sam, and Storch, H. H., Coal Hydrogenation Catalysts - Batch Autoclave Tests: Ind. Eng. Chem., vol. 42, February 1950, pp. 330-334.

## Bench-Scale Process Development

### Dependence of Coal Hydrogenation on Operating Variables

A full understanding of the mechanism by which coal is converted to oil and gas during its high-pressure, high-temperature hydrogenation must rest on a critical interpretation of the manner in which external variables influence the rate and course of the coal-hydrogenation reactions. Recent autoclave experiments[88] that extend the results of previous investigations on the kinetics of coal hydrogenation have resulted in the following observations.

In both the presence and the absence of an asphalt-free heavy-oil vehicle, the effect of hydrogen pressure on dry Bruceton coal at 450° C. for 1 hour (tin catalyst) is most important for initial pressures up to about 2,000 pounds per square inch. (Under reaction conditions, the hydrogen partial pressure is 2 to 2.5 times the initial pressure.) Above 2,000 pounds per square inch, under the reaction conditions used, an increase in initial hydrogen pressure played only a small role in determining the progress of the reaction. The hydrocarbon gas production and the hydrogen consumption are appreciably lower in the absence of vehicle. Part of this behavior is doubtless due to a production of gas by the hydrogenation of the heavy-oil vehicle.

In the range of 400° to 500° C., hydrogenation of dry Bruceton coal for 1 hour at 1,000 to 2,000 pounds per square inch hydrogen pressure (tin catalyst) showed that an increase in reaction temperature resulted in a decrease in asphalt content of the products. Corresponding increases in hydrocarbon gas production and in hydrogen consumption were also observed with increasing temperature. Within experimental error, the composition of the hydrocarbon gases produced was the same and was independent of temperature; this composition corresponded to approximately 30 percent $CH_4$, 25 percent $C_2H_6$, 25 percent $C_3H_8$, 15 percent $C_4H_{10}$, and 5 percent $C_5H_{12}$. It is interesting to note that coal can be almost completely liquefied (88 percent) under conditions where the principal hydrogenation product is asphalt, very little gas or oil being formed.

A study of the results obtained from the hydrogenation of dry Bruceton coal at a hydrogen pressure of 2,500 pounds per square inch and 400°, 430°, or 450° C. (tin catalyst) reveals that the liquefaction of coal proceeds rapidly in the absence of vehicle, even at 400° C.; at this temperature about 1 hour is sufficient to produce liquefaction greater than 85 percent. The hydrogenation of asphalt, however, is very slow at 400° C. At 430° C. the asphalt product is hydrogenated at an appreciable rate, and at 450° C. the asphalt hydrogenation proceeds almost as rapidly as does the liquefaction of coal. A variable contact-time unit for the hydrogenation of coal is shown in figure 24.

There has been a good deal of speculation as to the function of a vehicle in the coal-hydrogenation process. One of the most popular theories has been the suggestion that a vehicle, such as tetralin, functions by supplying hydrogen to the coal and that the high-pressure hydrogen present in the system serves to regenerate the tetralin. A study of the results obtained from the above experiments, as well as from those autoclave experiments[89] in which Bruceton coal was hydrogenated in the presence

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[88] Pelipetz, M. G., Kuhn, E. M., Friedman, S., and Storch, H. H., Studies of the Kinetics of Coal Hydrogenation: Bureau of Mines Rept. of Investigations 4546, 1949, 9 pp.

[89] Orchin, Milton, Goldbach, G. L., Wolak, Margaret, and Storch, H. H., Coal Hydrogenation: The Effect of Variations in the Coal-to-Vehicle Ratio: Bureau of Mines Rept. of Investigations 4499, 1949, 10 pp.

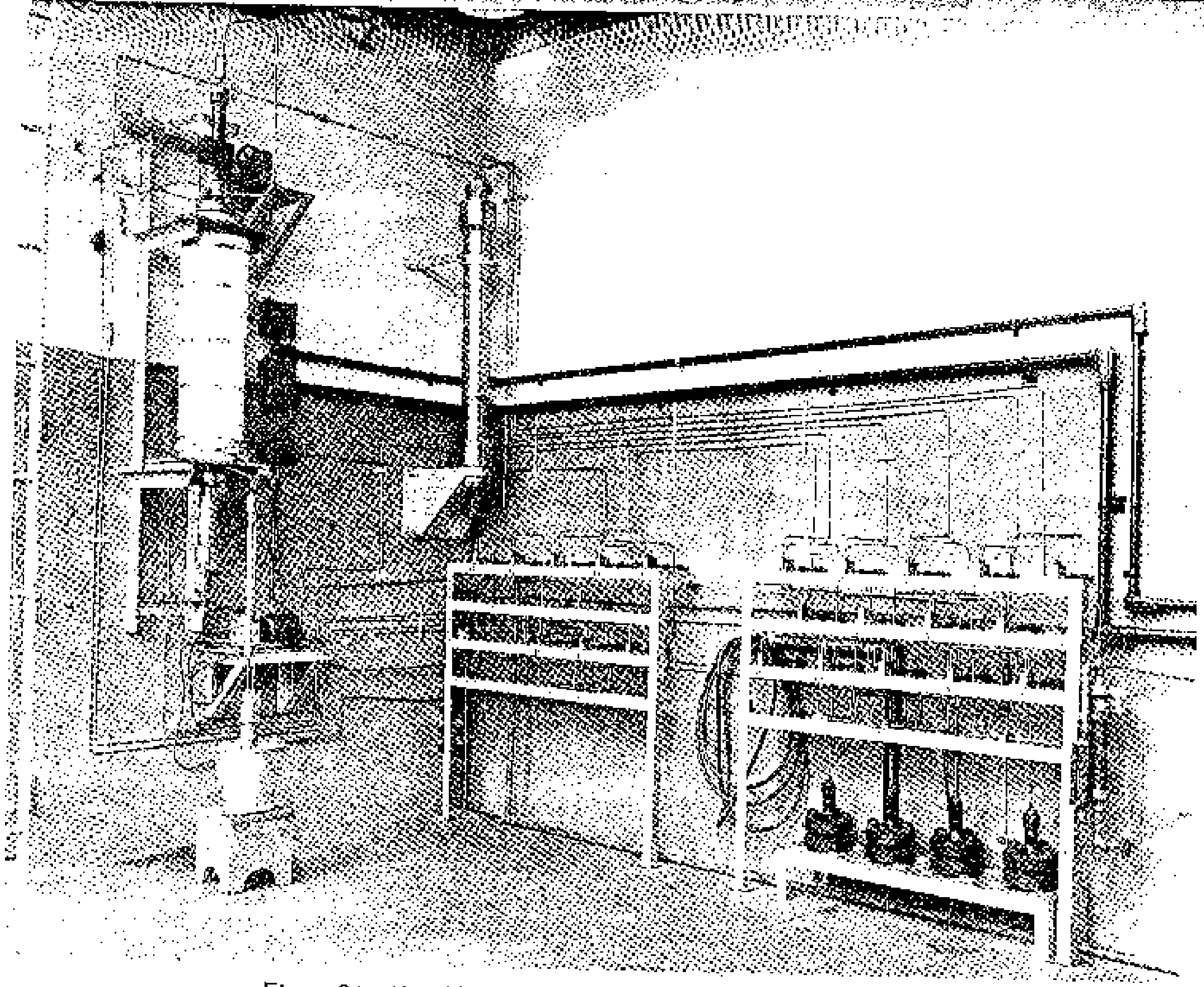

Figure 24. - Variable contact-time unit for hydrogenation of coal.

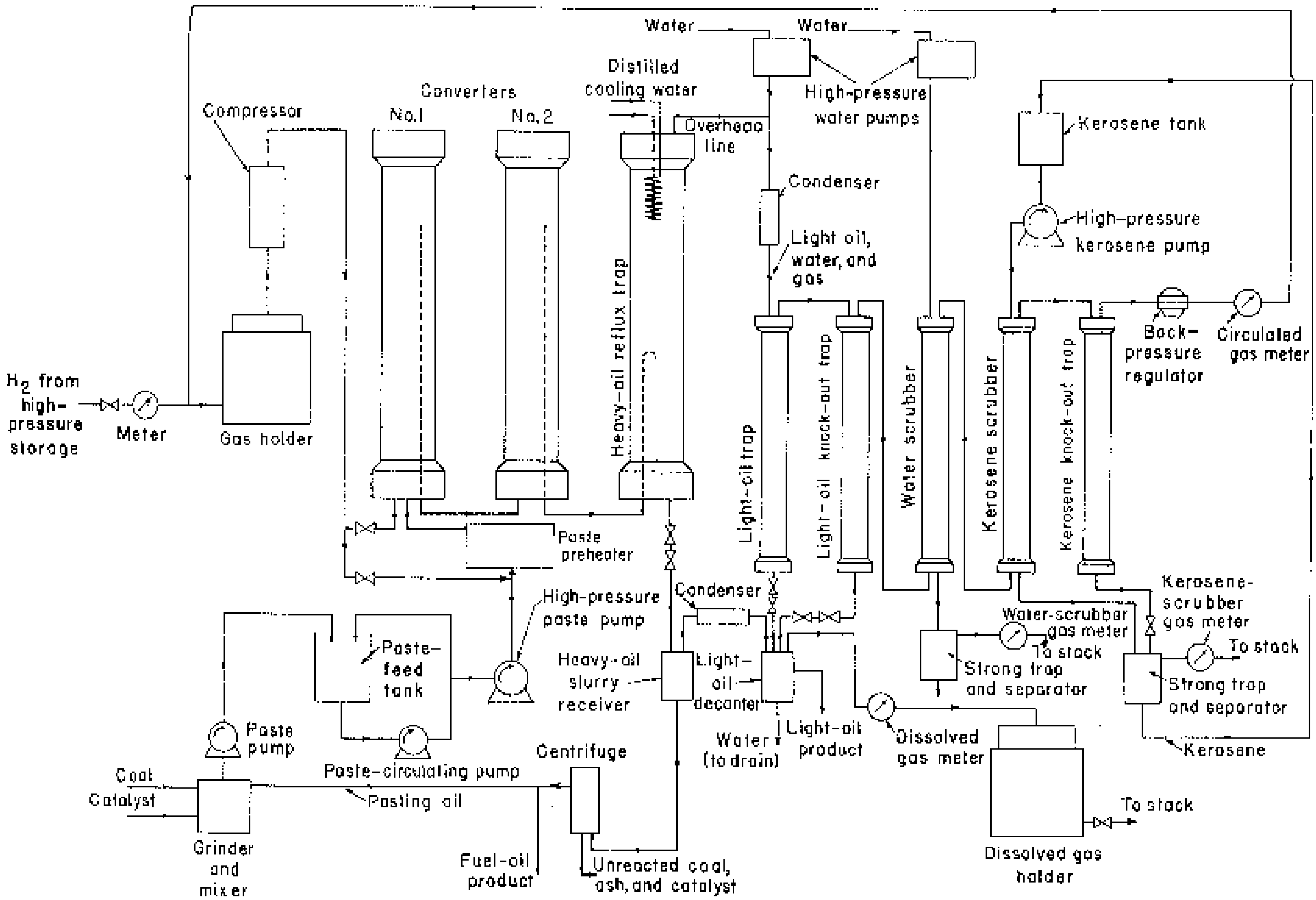

Figure 25. - Schematic flow diagram of coal-oil experimental plant.

of tetralin, largely substantiate the reaction mechanism described earlier. The experiments using tetralin indicate that the extent and rate of liquefaction of coal is not greatly dependent on the vehicle functioning as a hydrogen donor to the coal substance and that the slow step in the process is not likely to be the regeneration of such a vehicle. In the experiments using a heavy-oil vehicle, the progress of the liquefaction is almost unaffected by the presence of the heavy oil, but the rate at which asphalt is converted to lighter products is very much slower in the presence of this vehicle. This behavior will be very important in determining the relative merits of the conventional liquid-phase coal-hydrogenation process and one involving dry coal.

### Hydrogenation of Coal in the Absence of Solvents

German practices in the high-pressure hydrogenation of coal using liquid-phase vehicle (Bergius-I.G. process) have been thoroughly studied. Many features of this process indicate that potential advantages may be realized by effecting a reaction between coal and hydrogen in the absence of such solvents. In this manner, the equipment required to condition heavy-oil let-down for use as pasting or injection oil with the coal feed could be eliminated. Reaction space used by the oil portion of the coal-oil feed mixture could be used for the reaction of additional coal, and the removal of unreacted coal as a dry material, instead of a mixture with oil, would materially decrease the capital and maintenance cost of the hydrogenation plant. In addition, work in batch autoclaves has indicated that the heavy oil exercises a deleterious effect on the reaction.

Bench-scale hydrogenation of uncatalyzed Wyoming bituminous coal in an agitated or fluidized bed[90] resulted in an oil yield of 20 to 27 percent and hydrocarbon gas yield of 20 to 27 percent of the moisture- and ash-free coal at hydrogen pressures of 250 to 1,000 pounds per square inch and temperatures of 500° to 600° C. Hydrogenation of coal using a fluidized coal bed thus offers a possible means of dry coal processing at relatively low pressures. Products of the fluidized bed hydrogenation are oil, hydrocarbon gases, and a char residue suitable for use directly as fuel or for gasification to produce synthesis gas.

### Pilot-Plant Operations

A 9-month series of tests studying the manufacture of heavy fuel oil by high-pressure hydrogenation of Bruceton and Rock Springs bituminous coals was completed in the experimental liquid-phase pilot plant.[91] While one aim of this series of tests was the production of fuel oil meeting the requirements of the Bunker C or A.S.T.M.-6 grade, a sufficiently wide range of primary variables was investigated so that a comprehensive process variable study could be made. Included were the effects of contact time, reaction temperature, and concentration of the coal-oil feed paste on product viscosity, oxygen content, residual asphalt, sulfur content, and nondistillable soluble oil content for these coals using stannous sulfide and molybdenum trioxide as catalysts. A typical flow sheet of the pilot plant used in these studies is shown in figure 25. Results of the pilot-plant operations yielded, in addition to the above process variable study, tentative relationships between the several primary variables and hydrogen absorption, soluble oil yield, and light hydrocarbon-gas formation, as well as an approximate correlation of these parameters with product viscosity.

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[90] Clark, E. L., Pelipetz, M. G., Storch, H. H., Weller, S., and Schreiber, H., Hydrogenation of Coal in a Fluidized Bed: Ind. Eng. Chem., vol. 42, May 1950, pp. 861-865.

[91] Elliott, M. A., Kandiner, H. J., Dallenberger, R. H., Hiteshue, R. W., and Storch, H. H., Hydrogenation of Bituminous Coal in Experimental Flow Plant - Process Variable Study: Ind. Eng. Chem., vol. 42, January 1950, pp. 83-91.

Equilibria involving a single equation relating the product and reactant concentrations are readily treated by using the "degree of reaction" as a parameter. Where two or three equations are necessary to describe the concentration relationships in a system, this procedure may still be used, but the development and solution of the algebraic equations encountered are considerably more difficult. In really complex systems, such as that encountered in a continuous coal-hydrogenation process, the initial problem of selecting a consistent set of suitable chemical equilibria becomes very involved, and the labor of mathematical solution is almost prohibitive. The development of a simple method to accomplish this purpose[92] has greatly facilitated the analysis of complex equilibria existing among any number of chemical species in a single (gas) phase with or without the presence of a single solid phase.

## Separation and Identification of Products of Coal Hydrogenation

### Phenols in Coal-Hydrogenation Oils

Phenolic compounds of a wide variety are potentially available in huge amounts from coal-hydrogenation product oils.[93] It is, therefore, of considerable interest to determine the composition of the complex tar-acid fractions in which these phenols are found. Such mixtures are composed largely of homologous and isomeric phenols, and separation by the usual procedures of precise fractional distillation and fractional crystallization is difficult.

Nevertheless, these techniques, plus the invaluable assistance of qualitative and quantitative analyses[94] by means of the infrared spectrometer, have led to the characterization of those product oils distilling to about 200° C. Analysis of the higher-boiling fractions, however, is considerably more difficult because of the greater complexity of the tar-acid mixtures and because no infrared reference spectra are available. To gain an insight into the character of these very complex mixtures of acidic, aromatic hydroxy compounds, the countercurrent distribution technique, which was developed in other laboratories for the separation and analysis of small quantities of closely related compounds (such as antimalarial drugs and penicillin preparations), is being applied.

In the countercurrent distribution procedure, a mixture of phenols was distributed between two immiscible solvents in successive stages until separation into its components was achieved. During this investigation, it was observed that a relationship existed between partition coefficients and ionization constants of phenols and between these constants and the chemical configuration of phenol homologues.[95] In this way, it was possible to isolate individual or groups of closely related tar acids; 4-indanol, 5-indanol, and p-phenylphenol were isolated and identified as were 3-methyl-5-ethyl-phenol and o-phenylphenol. Thus, such a technique, when applied to a synthetic mixture of 3,5-xylenol, 2,5-xylenol, and 2,4-xylenol or a mixture of

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[92] Kandiner, H. J., and Brinkley, S. R., Jr., Calculation of Complex Equilibrium Relations: Ind. Eng. Chem., vol. 42, May 1950, pp. 850-855.

[93] Woolfolk, E. O., Orchin, M., and Dull, M. F., Phenols in Oil Obtained from Hydrogenation of Coal - Separation and Identification: Ind. Eng. Chem., vol. 42, March 1950, pp. 552-556.

[94] Friedel, R. A., Pierce, L., and McGovern, J. J., Infrared Analysis of Phenol, Cresols, Xylenols, and Ethylphenols: Anal. Chem., vol. 22, March 1950, pp. 418-420.

[95] Golumbic, C., Orchin, M., and Weller, S., Partition Studies on Phenols. I. Relation Between Partition Coefficient and Ionization Constant: Jour. Am. Chem. Soc., vol. 71, August 1949, pp. 2624-2627.

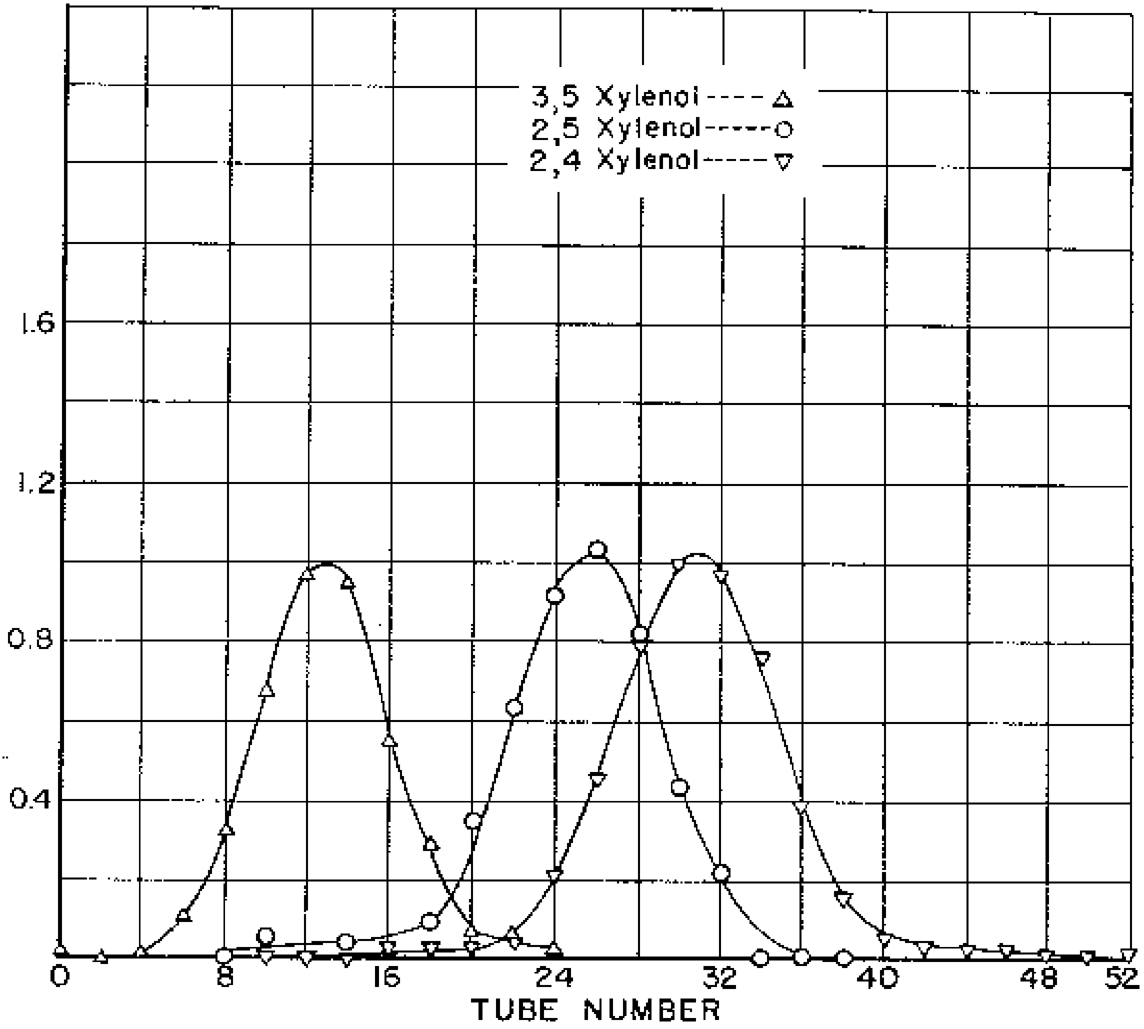

Figure 26. - Separation of xylenols: System, cyclohexane/phosphate buffer pH 11.08; sample, 10 mg. each.

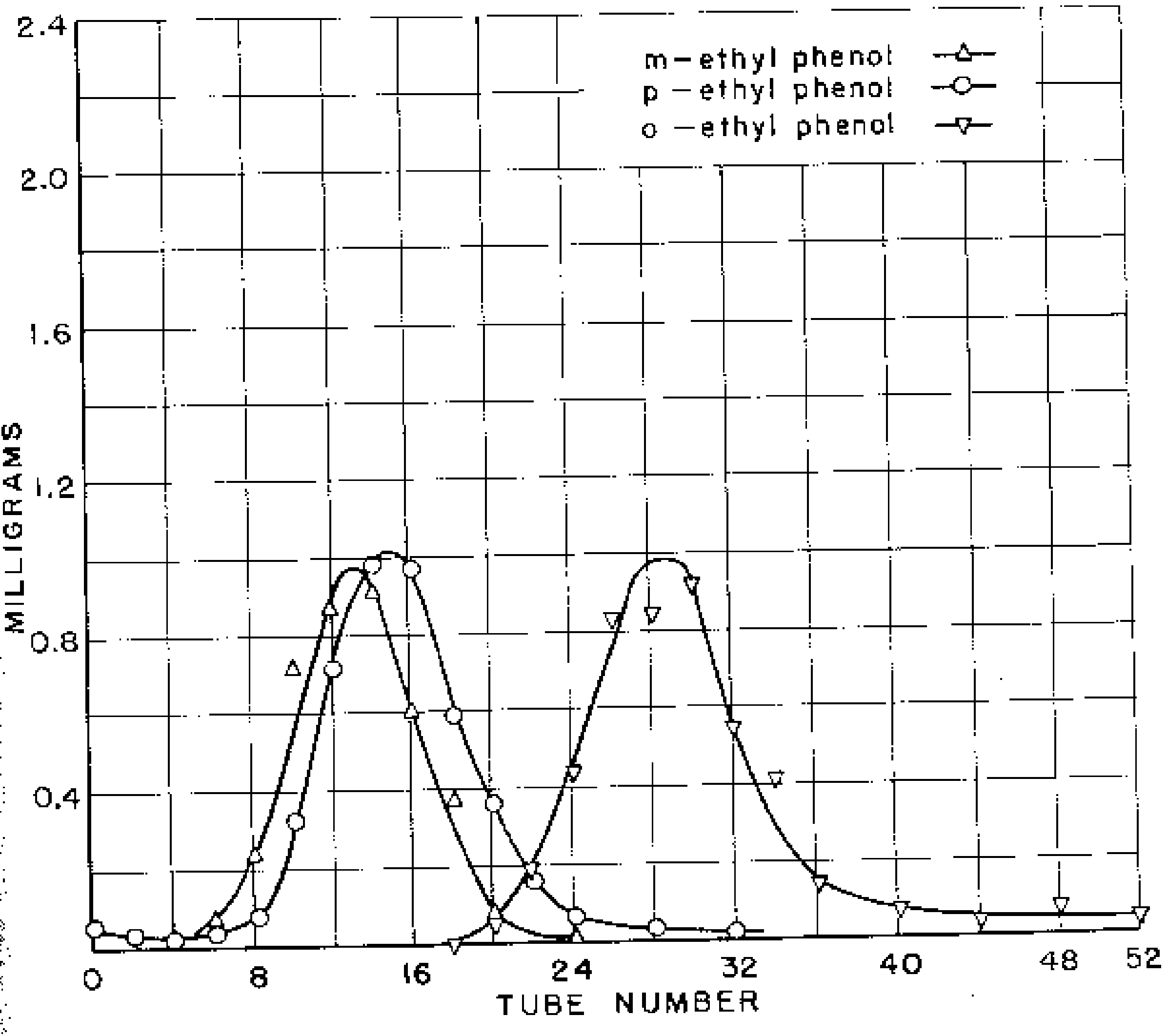

Figure 27. - Separation of ethyl phenols: System, cyclohexane/phosphate buffer pH 11.08; sample, 10 mg. each.

ortho-, meta-, and para-ethylphenols, shows[96] that 3,5-xylenol and ortho-ethylphenol can be readily separated from their respective mixtures. The shapes of the distribution curves (figs. 26 and 27) indicate that each compound distributes itself essentially independently of the others in accordance with the distribution law.

A study of the partition coefficients of dicycle phenols[97] demonstrated that the relative steric influence of methylene groups in six-membered rings is greater than that of five-membered rings. 4- and 5-indanol were isolated from the phenolic mixture obtained in the hydrogenation of Pittsburgh-bed (Bruceton) coal.[98]

The partition coefficients of 18 polynuclear compounds were also determined.[99] Partial saturation of ring structures and introduction of alkyl side chains increased the partition coefficients of parent compounds. Ring systems containing hetero nitrogen and oxygen atoms have lower partition coefficients than the corresponding carbocyclic structures. These effects permit application of the countercurrent distribution method to separation and analysis of polynuclear compounds. The countercurrent distributions of phenanthrene, acenaphthene, and a mixture of carbazole homologues were performed as typical examples. The countercurrent distribution technique permits the measurement of partition coefficients of the components of a mixture without isolating the individual compounds. These coefficients should be considered in the same category as the boiling point, melting point, and refractive index of a compound.

When the middle oils obtained from the hydrogenation of coal were hydrogenated at 450° and 475° C. in a stainless-steel autoclave in the absence of any added catalyst, very little of the phenolic material was converted to neutral products.[1] When the phenolic fraction of the middle oil was isolated prior to hydrogenolysis and then treated, more conversion of high-boiling to low-boiling phenols occurred, but this was accompanied by oxygen elimination and the production of about 20 percent neutral material.

## Characterization of Coal

The almost complete lack of knowledge of the chemical composition of coal in the past has greatly hindered the development of improved coal-hydrogenation processes. Earlier work has shown, however, that many of the polynuclear hydrocarbons found in

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[96] Golumbic, C., Partition Studies on Phenols. II. Separation of Isomeric Phenols by Countercurrent Distribution: Jour. Am. Chem. Soc., vol. 71, August 1949, pp. 2627-2629.

[97] Orchin, M., and Golumbic, C., Partition Studies on Phenols. III. Steric Effects: Jour. Am. Chem. Soc., vol. 71, December 1949, pp. 4151-4152.

[98] Golumbic, C., Woolfolk, E. O., Friedel, R. A., and Orchin, M., Partition Studies on Phenols. IV. Isolation of Indanols from Coal-Hydrogenation Oils: Jour. Am. Chem. Soc., vol. 72, May 1950, pp. 1939-1942.

[99] Golumbic, C., Separation and Analysis of Polynuclear Compounds by Countercurrent Distribution: Anal. Chem., vol. 22, April 1950, pp. 579-582.

[1] Orchin, M., and Storch, H. H., Hydrogenolysis of Phenols in Middle Oils from Coal Hydrogenation: Jour. Soc. Chem. Ind. (London), vol. 69, April 1950, pp. 121-122.

coal-hydrogenation oils may be explained in part by cyclodehydrogenation of less complex hydrocarbons. The attack on this problem was continued by aromatic cyclodehydrogenation[2] and auxiliary related studies.[3][4][5]

Research on the synthesis of fluoranthene and its derivatives led to the discovery of a method of production through the cyclohydrogenation of phenylnapthalene or derivatives thereof.[6] Fluoranthene is important in the dye industry where it is used for the preparation of certain intermediates. This method permits the use of readily available starting materials from which fluoranthene can be synthesized in a single direct step.

Examination of dispersions of a bituminous coal in phenanthrene by X-ray-powder photography revealed a characteristic diffraction pattern which was found to be identical with that given by partly amorphous abietic acid and aluminum and ferric abietates.[7] No reliable estimate of the concentrations of these constituents could be made, but qualitative observations indicated that they are minor constituents.

A German manuscript describing an investigation of the synthesis of branched-chain hydrocarbons in the laboratories of the Kaiser Wilhelm Institute for Coal Research was translated and published.[8] The paper contains data on the development of the catalyst for the isosynthesis, on the effect of temperature and pressure of operation, and on the composition of the products of the reaction.

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

### Reaction Mechanism Studies

### Metallic Carbides: The Magnetic Balance

A new method of synthesizing cementite ($Fe_3C$) that provides a good yield of product, not highly sintered or contaminated with free carbon, was found.[9]

The magnetic balance (fig. 28) makes it possible under certain circumstances to follow quantitatively the course of an isothermal reaction in the solid phase,

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[2] Orchin, M., Reggel, L., and Friedel, R. A., Aromatic Cyclodehydrogenation. IX. Further Studies on Ring Oxygen Compounds: Jour. Am. Chem. Soc., vol. 71, August 1949, pp. 2743-2746.

[3] Orchin, M. and Friedel, R. A., Structure of the Benzfluorenes and Benzfluorenones: Jour. Am. Chem. Soc., vol. 71, September 1949, pp. 3002-3005.

[4] Orchin, M., Synthesis of Perylene: U. S. Patent 2,478,205, Aug. 9, 1949.

[5] Orchin, M., and Wender, I., Apparatus for Measuring Gas Absorption or Evolution during Organic Reactions: Anal. Chem., vol. 21, July 1949, pp. 875-876.

[6] Orchin, M., and Reggel, Leslie, Synthesis of Fluoranthene and Its Derivatives: U. S. Patent 2,503,292, Apr. 11, 1950.

[7] Golumbic, C., Hofer, L. J. E., Peebles, W. C., and Orchin, M., Detection of Abietic Acid in Bituminous Coal: Jour. Soc. Chem. Ind. (London), vol. 69, April 1950, pp. 100-102.

[8] Pichler, Helmut, and Ziesecke, Karl-Heinz (translated by Brinkley, R., technical revision by Golumbic, N.), The Isosynthesis: Bureau of Mines Bull. 468, 1950, 39 pp.

[9] Hofer, L. J. E., and Cohn, E. M., Synthesis of Cementite: Jour. Chem. Phys., vol. 18, May 1950, pp. 766-767.

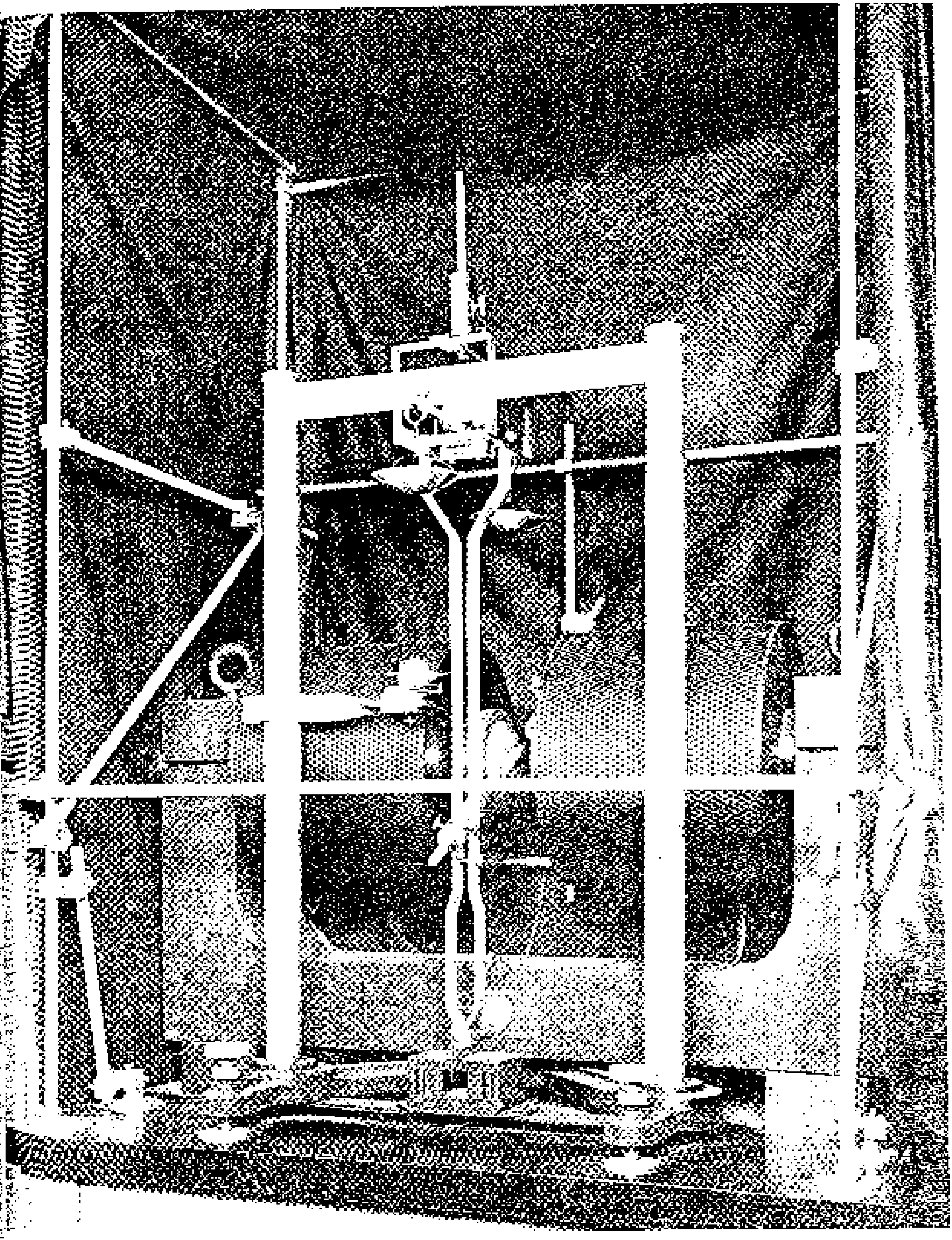

Figure 28. - Magnetic balance.

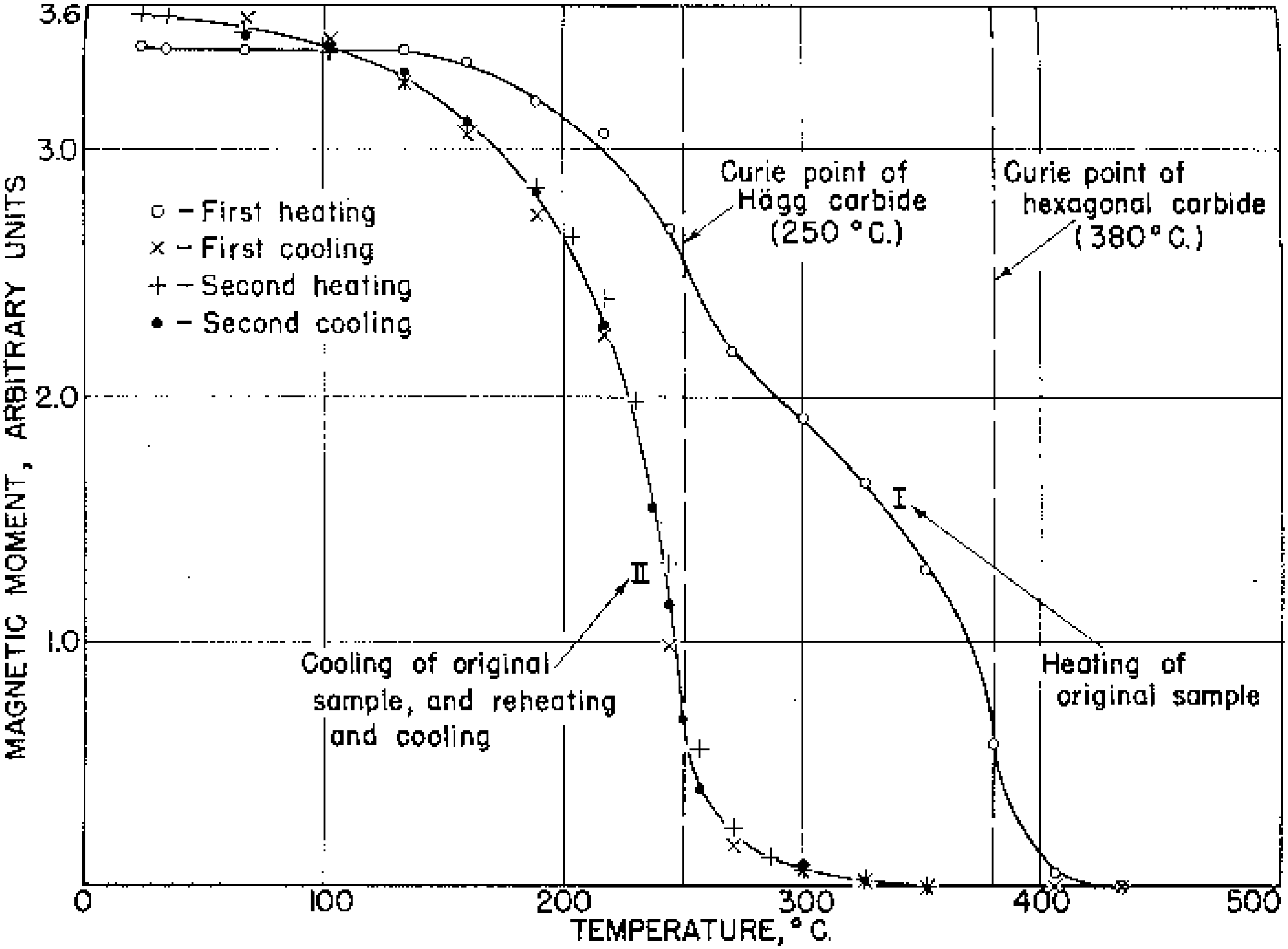

Figure 29. - Thermomagnetic curves showing the presence of the Hägg and hexagonal iron carbides in copper-promoted Fischer-Tropsch catalyst and the reversibility of the Hägg carbide curve.

by observing the change of the force exerted by a magnetic field on a sample that undergoes a chemical and simultaneous ferromagnetic change. This continuous physical analysis has been found to be especially useful in the case where a weak magnetic substance is converted to a strong ferromagnetic one (under the experimental conditions).10/ This method was invaluable in coordinating the widely scattered data for the various iron carbides, as reported by many investigators who carried out their studies along different lines.11/ Two of the properties obtained in this manner, the Curie point and the specific magnetization, can be determined from the thermomagnetic curve, a typical example of which is shown in figure 29. The specific magnetization is a characteristic property of a ferromagnetic phase, which decreases with increasing temperature and disappears at a temperature characteristic of that phase. This temperature is called the "transition temperature" or "Curie point." For practical purposes, the Curie point is usually defined as the point of inflection of a specific magnetization-temperature plot. Thus, the Curie point serves for qualitative identification, while knowledge of the specific magnetization makes quantitative estimates possible. Quantitative determination must be made at high field strengths where the ferromagnetic phases are magnetically saturated. High field strengths are also desirable for following reactions at constant temperature as a function of time. Besides the usual kinetic information, such studies can reveal modes of phase transition (continuous or discontinuous) which may not be readily accessible by any other means, and the method is suitable for following reactions in the solid state (where no changes in gas pressure occur) continuously and without interruption.

In applying this analytical procedure to the study of the isothermal decomposition of cobalt carbide, the rate of decomposition of cobalt carbide was measured by the change of magnetic force experienced by a decomposing sample between 300° and 360° C. in a constant magnetic field of constant field gradient. The measured values were then converted to percent cobalt carbide with the following two assumptions: (1) The initial magnetization of the sample was due to free cobalt, and (2) the force was directly proportional to the amount of cobalt present. The results showed that, in the range from about 80 to 25 percent cobalt carbide, the decomposition-time curves were linear, and hence the reaction was of apparent zero order in that range.

Reduced cobalt-thoria-kieselguhr catalysts produced increasing amounts of free carbon and decreasing amounts of cobalt carbide on carburization with carbon monoxide at increasing temperatures in the range 243° to 298° C.12/ At the high temperatures, the maximum amount of carbide is formed within the first 5 hours of carburization. Free carbon tends to make the catalyst inaccessible to further carbide formation.

Reaction-Rate Studies

The rate of synthesis of hydrocarbons on cobalt Fischer-Tropsch catalysts is dependent upon temperatures, operating pressure, composition, and flow of synthesis

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10/ Hofer, L. J. E., and Cohn, E. M., Studies of Ferromagnetic Materials: Cons. Eng. Corp. Recordings, vol. 4, March 1950, p. 5.

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