

A coal-hydrogenation asphaltene was examined for the Bureau by the Varian Corporation by proton magnetic resonance. Two peaks occurred in the fine structure. The small peak was attributable to a small number of hydrogen atoms and hydroxyl groups on benzenoid rings; the large peak to naphthenic, heterocyclic, and/or aliphatic  $\text{CH}_2$  and  $\text{CH}_3$  groups. There appeared to be no hydrogen on polynuclear condensed aromatic rings.

Whereas the infrared and magnetic methods yielded information about functional groups in coal, X-ray analysis indicated structural regularity. One may conceive of anthraxylon (the characteristic portion of coal) as being a polymer of small hexagonal rings (1 to 3 for Pittsburgh-seam coal) in partially oriented planar units. About 70 percent of the carbon atoms are contained in these layers. About 50 percent of the planar layers have no specific orientation toward each other (that is, they occur singly); the remainder occur largely in groups of two parallel layers separated by 3.6 A. X-ray analysis has not supported the existence of side chains in appreciable quantity. X-ray diffraction patterns of the benzene-insoluble residues from two products of coal hydrogenation were similar to those of coal.

#### Chemical Investigations on Coal

Cyclodehydrogenation Studies. - One fact frequently quoted as evidence for coal having a condensed polycyclic structure is the formation of polynuclear aromatic hydrocarbons on carbonization or hydrogenation. Studies on cyclodehydrogenation of mononuclear compounds (45, 46) were undertaken to show that polycyclic products can be formed under conditions similar to those existing during carbonization and hydrogenation of coal. A variety of reactions were found in which compounds having only single rings were converted to fused-ring structures. For example, 2-ethylbiphenyl, containing two unfused aromatic rings, readily yields fluorene and phenanthrene, each containing three fused rings. Accordingly, the formation of fused-ring systems from coal is not sufficient evidence for the existence of such structures in coal itself.

Solvation of Coal. - Experiments on pressure extraction of coal at 400° C. with a variety of solvents have suggested a correlation between degree of coal liquefaction and chemical structure of the solvent (45). High-boiling aromatic solvents, such as naphthalene, liquefied 20 to 30 percent of a bituminous coal; a readily dehydrogenated, hydroaromatic solvent, such as tetraline, liquefied about 50 percent; and hydroaromatic compounds containing a phenolic group, such as o-cyclohexylphenol, liquefied more than 80 percent. Under these conditions, solvation probably involves mild hydrogenolysis of carbon-to-oxygen linkages by hydrogen from hydroaromatic solvents. With the hydroxylated solvents, there is probably also dissociation of the coal or coal products, with hydrogen bonding of the fragments to the solvent. In the presence of high-pressure hydrogen, liquefaction of coal is readily achieved with vehicles containing a hydroxyl group attached to an aromatic ring.

Tests were made of the effectiveness of a number of polynuclear compounds containing three or more condensed rings, used at their atmospheric boiling points, in the extraction (34, 44) of a high-volatile A bituminous coal (Pittsburgh seam). Phenanthrene extracted 95 percent of the coal at 340°, whereas

anthracene extracted only 24 percent at 354° C. The ineffectiveness of anthracene did not appear to be due to chemical interaction with or to strong adsorption on the coal surfaces, because the anthracene could be recovered quantitatively from the extracts in the same manner as good solvents, such as phenanthrene.

Phenanthrene dispersed only about 25 percent of a subbituminous coal or lignite, whereas  $\alpha$ -naphthol dispersed about 80 percent of either bituminous or subbituminous coal.  $\beta$ -naphthol dispersed only about 17 percent of a subbituminous coal and about 78 percent of a bituminous coal.

Optical Activity in Oils From Coal. - Several coal-hydrogenation oils and a low-temperature lignite tar were found to contain optically active constituents. Fractions from these sources gave both positive and negative rotations. Optical activity has been found chiefly in the paraffin-naphthenic and hydroaromatic portions of the various neutral oils; little or no activity was found in the acidic or basic fractions. The oils obtained by treatment of coal with hydrogen in the presence of added catalyst contained less optically active material than the oils obtained from low-temperature tar. However, a fraction with high specific activity has been isolated from a Louisiana, Mo., coal-hydrogenation middle oil.

Optical activity was found in lignite-tar fractions which boil as low as 135° C. (275° F.). Mass spectrometric analysis and the physical properties of this material indicated that the optical activity was due to a C<sub>8</sub> naphthenic hydrocarbon, probably a cyclohexane derivative.

Further studies were undertaken on the relationship of optical activity to coal origin and coal structure and the usefulness of polarimetry in determining the nature and extent of the treatment of coal.

Chars Produced by Pyrolysis of Organic Substances. - A number of organic compounds, natural products, and synthetic polymers were pyrolyzed in a bomb under carefully controlled conditions at 200° to 400° C. The objectives were (1) to study the mode of formation and structure of chars which resemble coal and (2) to prepare ash-free model substrates for coal investigations.

With a few exceptions, only carbohydrates and compounds structurally derived from them yielded chars at 300° C. A carbonyl group was essential for char formation at 300° C., but the number of carbon atoms was not important. Dihydroxyacetone, 2-desoxyglucose, glucuronolactone, and arabinose yielded chars at 300° C., while glycerol and sorbitol did not. At 400° C. these materials, as well as glycerol and sorbitol, produced chars that resembled bituminous coal in infrared spectra, ultimate analyses, and solubility in common organic solvents. X-ray diffraction patterns and nonaqueous acid-titration curves of several 400° C. carbohydrate chars resembled those of bituminous coal. Compounds containing aromatic rings were more stable at these temperatures; although some of these compounds yielded chars at 400° C., the infrared spectra of the chars showed evidence of original structure. Catalysts such as stannous chloride and aluminum chloride increased the coal-like character of carbohydrate chars formed at 200° and 250° C., apparently by a mechanism involving acid catalysis.

## Microbial Study of Structure of Coal

A project initiated in 1954 has been concerned with studies of the structure of carbonaceous substances, such as coal, by the analysis of products obtained from them by microbial action. Studies included the microbial degradation of high-molecular-weight organic substances with the formation of low-boiling products. Since microorganisms function under mild conditions, cleavage products produced from coal by microbial action might more nearly represent the coal molecule than products from the more drastic methods of chemical or physical degradation.

Evidence accumulated to date indicates that:

1. A definite microflora is associated with coal.
2. The wax extracted from coal by methanol is bacteriostatic; the active fraction has been concentrated by fractional precipitation.
3. Polynuclear compounds containing as many as nine condensed rings are attacked by microorganisms.
4. Microorganisms degrade phenanthrene by attacking first an end ring, as indicated by intermediates that have been isolated.

### Autoclave and Related Experiments on Coal Hydrogenation

#### Amenability of Naturally Occurring Carbonaceous Materials to Liquefaction by Hydrogenation

A number of American coals were investigated in autoclave studies and found suitable for the production of synthetic liquid fuels by hydrogenation. Colorado, Wyoming, Illinois, Kentucky, and Pennsylvania coals yielded about 70 to 80 percent of benzene-soluble oils in iron-catalyzed reactions at 450° C. (842° F.), initial (cold) hydrogen pressures of 4,000 p.s.i. and contact times of 1 hour. Similar results were obtained with a North Dakota lignite and with gilsonite, a naturally occurring asphalt. This has been an extension of previous Bureau work on the liquid-phase assays of bituminous, subbituminous, and lignitic coals (57). Experiments were conducted also on the feasibility of producing synthetic fuels by hydrogenation of a lignite from the South Arcot district of India. The behavior of this lignite under hydrogenation conditions closely resembled that of the American Rock Springs, Wyo., coal.

#### Action of Catalysts in Liquid-Phase Hydrogenation

Semiempirical tests of many catalysts have been made in batch-autoclave experiments in a search for cheaper and more effective catalysts for the hydrogenation process (64). The mechanism by which the most active catalysts operate was also studied. This work led to formulation of a descriptive theory of coal hydrogenation (59). It was postulated that, in the presence of tin chloride, coal (or asphalt) is thermally split to form reactive fragments, the cracking being catalyzed by halogen acids. The fragments either

polymerize to form benzene-insoluble products or are stabilized by the addition of hydrogen to form soluble products. The hydrogenation stabilization is catalyzed by tin. Although refinements of the theory are required, it has considerable value in suggesting the design of future experiments.

The method of addition and the degree of distribution of catalysts were found to be of importance in autoclave work (61). A number of catalysts were much more active when impregnated on the coal from aqueous solution than when added as powders to the powdered coal. The ball-milling of coal and catalyst together was of intermediate effectiveness. These experiments emphasized the role of catalyst distribution in determining catalyst activities, and showed the need for caution in interpreting the results of empirical catalyst-testing experiments in terms of intrinsic catalyst activities.

Studies have been made of the role of the inorganic constituents of coal in hydrogenation. Experiments have suggested that some inorganic constituents, present in whole coal but not in anthraxylon, acted as a moderately active catalyst for hydrogenation (60). Also, several reports claimed the desirability of neutralizing basic constituents of coal ash before hydrogenation (56, p. 1759). Bureau of Mines work confirmed the effectiveness of adding sulfuric acid in conjunction with an ammonium molybdate catalyst (60). Other acids were not effective, indicating that the action was not simple neutralization.

#### Solvation and Hydrogenation of Coal

Experiments on the pressure extraction of coal at 400° C. with a variety of solvents have suggested a correlation between the degree of coal liquefaction and the chemical structure of the solvent (47). Under these conditions, solvation probably involves a mild hydrogenolysis of carbon-to-oxygen linkages by the hydrogen available from hydroaromatic solvents, dissociation of the coal or of primary products from the coal, and hydrogen bonding with phenolic solvents. These results may have an important bearing on the role of vehicle oils in coal-hydrogenation processes.

#### Kinetic Studies

A study has been made of the effect of operating variables on the batch-autoclave hydrogenation of coal to asphalt, oil, and gaseous hydrocarbons (50). The variables studied were hydrogen pressure, temperature, contact time, and effect of a vehicle. Investigation of the relationship between catalyst activity and hydrogen pressure led to a useful mathematical expression of reaction rates and catalyst activity as a function of hydrogen pressure (51).

Batch-autoclave study of the kinetics of hydrogenolysis of bituminous coal anthraxylon (63) covered a range of yields from 80 percent asphaltene and 8 percent oil at one extreme to 6 percent asphaltene and 76 percent oil at the other. The results furnished evidence that asphaltene was an intermediate product in coal hydrogenation, and provided quantitative data on the rates of coal-to-asphaltene and asphaltene-to-oil reactions. Conversion of coal to liquid and gaseous products at 400° C. (752° F.) appeared to be a first-order reaction with respect to the benzene-insoluble matter remaining.

A kinetic study was made also of the conversion of asphalt to lower molecular weight material by hydrogenation (62). The conversion of asphalt was found to be a first order reaction with respect to asphalt remaining and apparently also with respect to hydrogen pressure over the range of 400° to 440° C. (752° to 824° F.). The apparent activation energy in the range 430° to 440° C. was 36 kcal. per mole. ~~The kinetics of the hydrogenation of lignite was investigated at 400° C. and initial pressures (cold) of 1,000-4,000 p.s.i.~~ (18). The main product was asphaltene. Conversion of benzene-insoluble matter followed a first order rate law with respect to benzene insolubles remaining.

#### Hydrogenation of Low-Temperature Tar

A batch-autoclave study has been made of the hydrogenation of low-temperature-tar pitch. Experiments conducted for 1 hour, with an initial pressure (cold) of 3,000 p.s.i. and without a catalyst, showed an increase in light oil yield and a decrease in asphaltene content of the residual oil as the reaction temperature increased from 450° to 500° C. (842° to 932° F.). Varying the initial hydrogen pressure from 1,000 to 3,000 p.s.i. increased the heavy-oil yield and decreased the asphaltene content of this fraction. The results suggest that an operating pressure of 3,000 or 4,000 p.s.i. would be satisfactory in a continuous tar-hydrogenation plant.

Iron catalysts appeared to have very little activity at 475° C. and an initial pressure of 3,000 p.s.i. Activated-carbon catalysts had appreciable cracking activity. Activated carbon impregnated with a molybdenum catalyst was still more active and produced higher light-oil yields.

#### Variable Contact Time

A study on the effect of very short contact times in hydrogenation was made with uncatalyzed Rock Springs, Wyo., coal. A special reactor (fig. 40) was constructed containing a series of 13 ledges spaced about 1 inch apart. Riding closely on each ledge was a scraper attached to a central shaft. Coal was fed by a brush feeder from a hopper onto the top ledge; it was swept by the rotating scraper to the next lower ledge and similarly from ledge to ledge and finally into an air-cooled receiver. Contact time from the entrance of the coal to its exit was governed solely by the speed of rotation of the central shaft and was thus independent of the feed rate, which was held at 80 to 120 grams of coal per hour.

Experiments were made at 500, 1,000, and 2,000 p.s.i.g.; at 400°, 450°, and 538° C. (752°, 842°, and 1,000° F.); and at four contact times, 0.12, 1.6, 7.2, and 14.5 minutes. Most of the conversion at any pressure and temperature occurred within 0.12 minute (table 8), and the total conversion then asymptotically approached a maximum in about 3-6 minutes.

Reasonably good correlations were obtained between conversion and the hydrogen, carbon, and oxygen remaining in the benzene insolubles. The greater the conversion, the poorer the benzene insolubles became in hydrogen and oxygen. These observations agreed with the fact that carbonaceous materials with low concentrations of oxygen and hydrogen, such as anthracite or graphite, are difficult to hydrogenate.

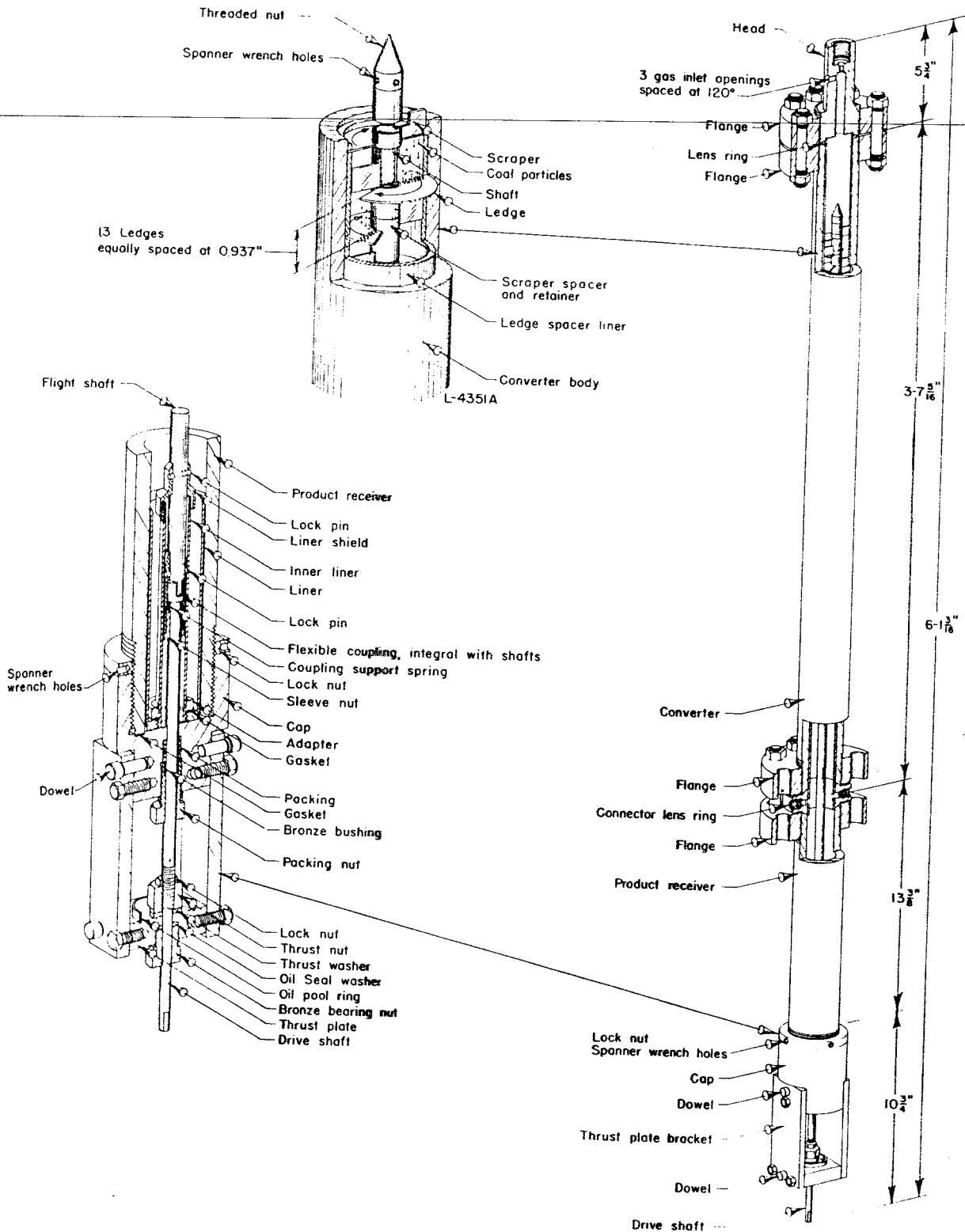


FIGURE 40. - Design of Reactor for Hydrogenating Coal During Known Contact Times.

TABLE 8. - Hydrogenation of Rock Springs coal as affected by contact time, pressure, and temperature

Pressure, p.s.i.g.	Conversion in 0.12 minute, percent, at temperatures indicated			Maximum conversion (usually in less than 7 minutes), percent, at temperatures indicated		
	400° C.	450° C.	538° C.	400° C.	450° C.	538° C.
500.....	14.5	20	30	17.5	26	40
1,000.....	12	20	28	20	28	46
2,000.....		17	36		33	50

#### Characterization of Coal-Hydrogenation Products

Early in the program a laboratory was set up for separation and identification of the complex products from synthetic fuels processes.

#### Direct Determination of Oxygen

The oxygen content of oils from coal hydrogenation is a useful index of the efficiency of primary conversion and subsequent refining. Oxygen usually is estimated by difference after all other constituents are determined. However, this method is objectionable because it is slow, and the cumulative errors of all the individual determinations may produce a substantial error in the oxygen-by-difference value. Therefore, a rapid direct semimicro method was developed for determination of oxygen in organic substances (37).

Samples are pyrolyzed in a closed system and the products swept by a stream of dry oxygen-free nitrogen through a carbon-packed reaction tube at 1,120° C., which converts oxygen-containing fragments quantitatively into carbon monoxide. This is oxidized to carbon dioxide, absorbed in alkali, and the excess back-titrated with acid after precipitation of the carbonate with barium chloride. Analyses of substances of known oxygen content indicated that accurate results were obtained over a range of 0.05 to 50 percent oxygen, utilizing sample weights of 15 to 350 mg., in as little as 45 minutes.

#### Separation and Analysis of Higher Boiling Oils From Coal Hydrogenation

The oils obtained by hydrogenation of bituminous coal are complex mixtures of paraffinic, naphthenic, and polynuclear compounds. These oils were characterized by distillation, chromatography, and determination of physical constants (25); isolation of pure compounds was generally incidental to the analysis. Some of the polynuclears isolated (68) were: Anthracene, phenanthrene, pyrene, chrysene, 4,9-dimethylpyrene, and coronene (43). By chromatography on silica gel (68) a wax fraction could be isolated from the heavy oil obtained by hydrogenation.

Methods were developed for the separation and identification of polynuclear hydrocarbons; 1- and 2-methylnaphthalenes were separated by azeotropic distillation (24), fluoranthene and chrysene were separated by codistillation (19), and polynuclear compounds were separated and analyzed by countercurrent

distribution (33). A useful procedure was also developed for the identification and purification of aromatic polynuclear compounds using molecular complexes with 2,4,7-trinitrofluorenone (48).

### Spectroscopic Analysis of Coal-Hydrogenation Products

Qualitative and quantitative analyses of phenols in carbon disulfide solution were made by infrared spectrometry (31). Mass spectrometry has been applied to type analyses (9) of the C<sub>6</sub>-C<sub>8</sub> paraffin-naphthene fractions from coal-hydrogenation oils (29). Complete analysis of individual components was too laborious, but the short-cut method furnished analyses of five types of mixtures: Total paraffins, mono- and poly-substituted cyclopentanes, and mono- and poly-substituted cyclohexanes. The polysubstituted cyclopentanes were further classified into three types (29).

A mass spectrometric method was devised for analysis of components up to C<sub>9</sub> in total liquid products from coal hydrogenation. The products were fractionated into wide-boiling-range cuts, and specific analyses by the mass spectrometer made for benzene, toluene, total C<sub>8</sub> aromatics, and approximate analyses for total C<sub>9</sub> aromatics, total C<sub>10</sub> aromatics, tetralin, naphthalene, total paraffins, and total naphthenes.

In the presence of up to 99 percent of hydrogen, mass spectrometric analyses can be made for many gaseous compounds, including nitrogen, oxygen, carbon dioxide, methane, ethane, propane, butanes, pentanes, cyclopentanes, hexanes, and cyclohexanes. Ultraviolet spectra from vapors of aromatic molecules, such as benzene, toluene, xylenes, and ethylbenzene, contain much more fine structure than spectra from liquids, so more reliable quantitative and qualitative analyses could be obtained from the vapor spectra. A method of analysis based on this principle has been developed.

### Characterization of Tar Acids From Coal-Hydrogenation Oils

The tar-acid fraction of the n-hexane-soluble portion of the liquid product from hydrogenation of Pittsburgh-bed (Bruceton) coal was isolated by methanolic potassium hydroxide (Claisen's alkali) extraction of the benzene solution of the oil (66, 67). Tar acids comprised 9.4 percent by weight of the n-hexane-soluble oil, or 5.2 percent of the total oil produced. The tar acids were divided into 136 fractions by distillation, and the refractive indexes of all fractions and the densities of the higher boiling fractions were determined. Careful interpretation of the data on physical constants would permit selection of fractions rich in any desired phenol occurring in the oil.

Before active work on the fractions, extensive preliminary experiments were conducted on model compounds. Study of the distribution (partition) of various phenols between cyclohexane and a buffered aqueous phase led to the development of rules and formulas relating partition coefficient to ionization constant and also to better understanding of the factors governing extractability of phenols. The differences in partition coefficients of isomeric phenols permitted application of the countercurrent distribution method to their separation and to determination of their purity. Infrared spectra were determined