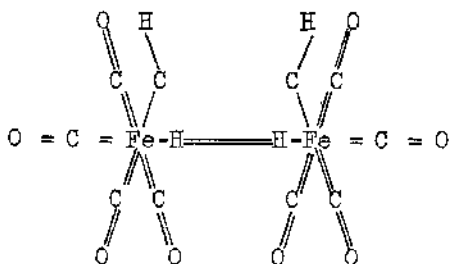


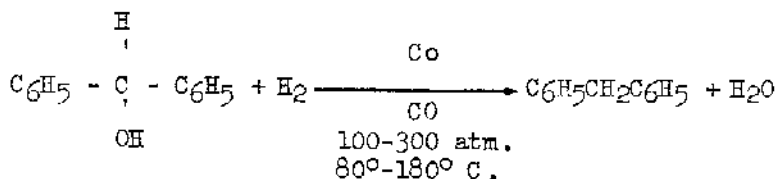
have been assumed to represent possible intermediates in the Fischer-Tropsch process. The reaction of acetylene with iron pentacarbonyl in aqueous alkali at room temperature and atmospheric pressure has yielded a stable complex with the probable structure



(II)

The iron complex (II) differs from (I) in that it contains 2 hydrogens bonded to metal, 1 of which has been shown to be acidic. The fact that this hydrogen is replaceable by alkali may provide information concerning the role of alkali in the Fischer-Tropsch process. Complex (II) is an unusual entity, as it contains, in one molecule, catalytic metal, alkyl substrate, and hydrogen and carbon monoxide necessary for chain lengthening.

In an attempt to find a hydrogenation reaction that occurs in the presence of large amounts of carbon monoxide, benzhydrol was reacted with synthesis gas in the presence of catalytic amounts of dicobalt octacarbonyl. A quantitative yield of diphenylmethane was obtained without side-reactions according to the following equation:



The kinetics of the reduction of benzhydrol and paranuclear-substituted benzhydrols at 150 to 300 atmospheres of synthesis gas and 95° to 180° C. was studied. Polar solvents and electron-releasing substituents in the para positions of benzhydrol increased the reaction rates. Further study of the nature of the electron transfers in this homogeneous system should yield information concerning the nature of hydrogen transfer in heterogeneous systems.

Synthesis of Liquid Fuels by Hydrogenation of Coal

High-Temperature Coal Hydrogenation

The single-step process for direct conversion of coal to gasoline differs from the conventional process in that the liquid- and vapor-phase stages are combined in one unit operating at temperatures above 500° C. with a large quantity of active catalyst. The combination of high temperature, pressure, and catalyst concentration should produce a low-boiling recycle oil and thus improve the overall yield of liquid by minimizing losses of oil during removal of solids. Continuous, bench-scale equipment was used for exploratory work, and a pilot plant was built for developing operating technique and reactor design.

Bench-scale work was directed toward a study of the effect of flow rates of gas and paste upon the extent of reaction and type of products. These experiments were performed in a 32-foot coil of 1/8-inch inside diameter wound in a helix of 4-inch diameter. Rock Springs, Wyo., coal, impregnated with 1 percent molybdenum after neutralization with sulfuric acid, was used. Coal paste was prepared by mixing in a colloid mill (see fig. 7) 40 weight-percent of coal with 60 of oil having a distillation range of 250° to 312° C. All tests were made by passing the reactants through the coil without recycling at 535° C. and a pressure of 8,000 p.s.i.g. An eightfold change in paste rate at constant gas flow did not affect conversion or type of products. About 95 percent of the coal was converted to liquids and gases. Yields of gasoline, based on moisture- and ash-free feed, amounted to 17 percent and of residual oil (boiling above 204° C.) and hydrocarbon gases to approximately 73 and 7 percent, respectively. The product oil had an appreciably higher boiling range than the original vehicle oil; its 90-percent point was about 350° C. The 0° to 160° C. cut contained about 16 percent paraffins, 23 percent naphthenes, 4 percent benzene, and less than 1 percent asphaltenes. A sixfold change in gas velocities at a constant paste rate gave essentially the same results. However, gas velocities did affect the gasoline content of the product oil, which increased with decrease in gas velocities. Apparently these changes were due primarily to hydrogenation of vehicle oil rather than coal. Results obtained when vehicle oil alone was hydrogenated indicate a similar relationship between gasoline content and gas rate. Thus, the heavier fractions of oil must be produced from coal. Recycle studies will be made to evaluate properly the yield of products from coal.

The data support the following hypothesis on the events occurring in the tubular reactor: Slug flow of coal-oil slurry probably occurs at the inlet of the reactor. Vehicle oil is vaporized almost immediately. The vapors attain a velocity comparable to that of hydrogen and are hydrogenated in the vapor phase to gasoline and higher boiling hydrocarbons. During flashing, coal is converted in a matter of seconds to primary products, such as asphaltenes and heavy oils. These fractions are pushed through the tube and form a rather thin film on the walls. Here, they undergo hydrogenation to lighter fractions and are swept out as vapor. A steady-state film should thus be established, the thickness of which should be a function of paste rate. Hence, in this unit virtually no control of contact time of product oil with hydrogen can be achieved.

The present work indicates that coal can be rapidly converted into primary products by direct hydrogenation at elevated temperatures. Components of these primary materials, such as asphaltenes and heavy oil, will be separately hydrogenated under identical conditions to determine more closely the course of this reaction at high temperatures.

Attempts have been made to operate the high-temperature process in a pilot plant to obtain data under steady-state recycle conditions. The available liquid-phase pilot plant was modified; the present plant has a reactor with 3-inch inside diameter and is designed for operation at 8,000 p.s.i.g. and 525° C. The same coal, vehicle oil, and catalyst types were used as in bench-scale studies. Hourly flow rates were about 25 pounds of paste and 500 cubic feet of gas. The major difficulty has been dissipation of the high heat of reaction. Unsuccessful attempts were made to moderate this difficulty by establishing a longitudinal temperature gradient in the reactor, by lowering catalyst concentration, and by using a higher molecular-weight vehicle oil. Internal cooling by recycle hydrogen in conjunction with external heating resulted in moderately successful operation at 480° to 510° C. with results similar to those obtained in the bench-scale unit. However, the temperature was not uniform throughout the reaction zone. Operations were limited in that only the upper third of the reactor could be utilized as reaction space, whereas the lower two-thirds served as a preheater. Cold hydrogen was injected into the reaction

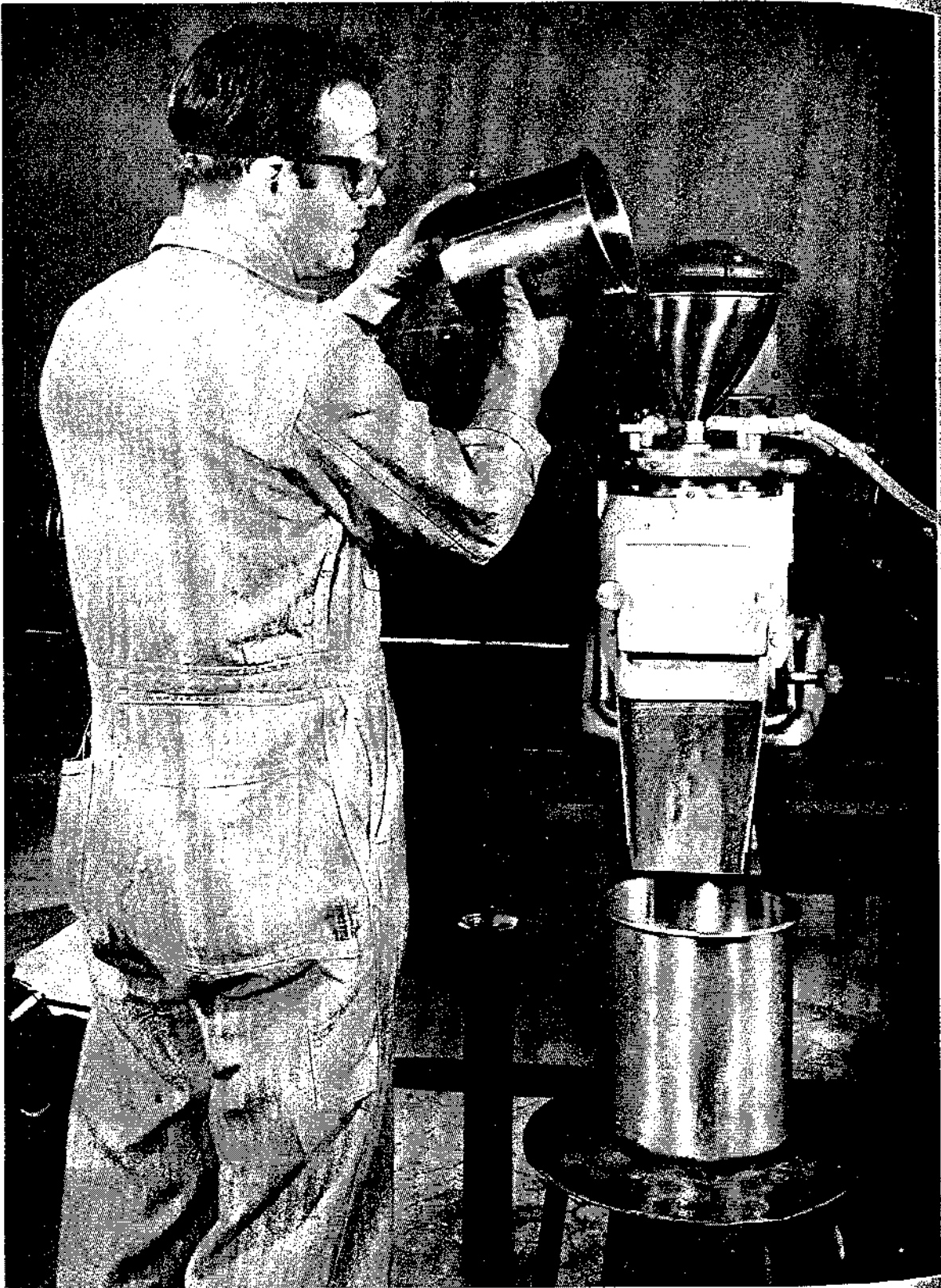


Figure 7. - Colloid mill.

space by means of a high-pressure booster compressor (see fig. 8) automatically controlled by the temperature of the reaction zone. The height of the reaction zone could not be increased without obtaining excessively high-temperatures (above 700°C .). Apparently this reactor is inadequate for both preheating the reactants to the initial reaction temperature (425°C .) and then dissipating the heat of reaction. Control of temperature is difficult to maintain in a single reactor, primarily because no clear line of demarcation exists between the heating and cooling zones. This difficulty can probably be solved by using two separate systems, a preheater and a reactor, which are being designed. Reactants will be heated rapidly to 425°C . and discharged into an insulated reactor provided with inlets for injecting cold gas. Thus, the heat of reaction will be the sole source of heat in the second unit, and excess heat will be removed by cold hydrogen. External furnaces will be employed only for minimizing heat losses.

An economic evaluation of the high-temperature coal-hydrogenation process was made by the Oil-Shale Engineering Branch at Rifle, Colo. The cost study was based on modifying a modernized Bergius coal-hydrogenation plant on which past evaluations have been made. It included an analysis of the independent effect of major process variables on the economics.

Structure of Coal

Preparation of Coallike Chars

Cellulose and sucrose are known to form coallike chars on being heated to elevated temperatures. Char formed by heating cellulose to 400°C . has an infrared spectrum that closely resembles that of coal. Work has been started on the formation of coallike chars from other compounds to determine the structural requirements for forming such chars and to study the mechanism of their formation. This investigation may contribute information on the process of coalification and on the structure of coal.

All carbohydrates studied formed chars on heating:

Arabinose	A 5-carbon aldose
Glucose	A 6-carbon aldose
Fructose	A 6-carbon ketose
Sucrose, maltose	Nonreducing disaccharides
Raffinose	A nonreducing trisaccharide
Cellulose	A glucose polymer

Chars formed at 400°C . had infrared spectra similar to coal; those formed at 300°C . were not completely coallike.

When the carbonyl group in glucose or fructose is hydrogenated to a hydroxyl group, no char is formed on heating. Inositol, a saturated 6-carbon-ring compound with 1 hydroxyl group on each carbon, also does not form a char. Thus, the presence of a carbonyl group or an incipient carbonyl group is necessary for charring of carbohydrate-like materials. That the property of forming coallike chars is fairly specific was shown by the fact that, of a large number of compounds structurally similar to the carbohydrates examined, only those with 1 hydroxyl group per carbon and 1 carbonyl group per molecule formed a char on heating. Lignin, which is not a carbohydrate but may have been derived from cellulose, also forms a coallike char on heating.

The same relationship between structure and char formation has been found upon charring by acids. The mechanism of such charring of organic materials is being

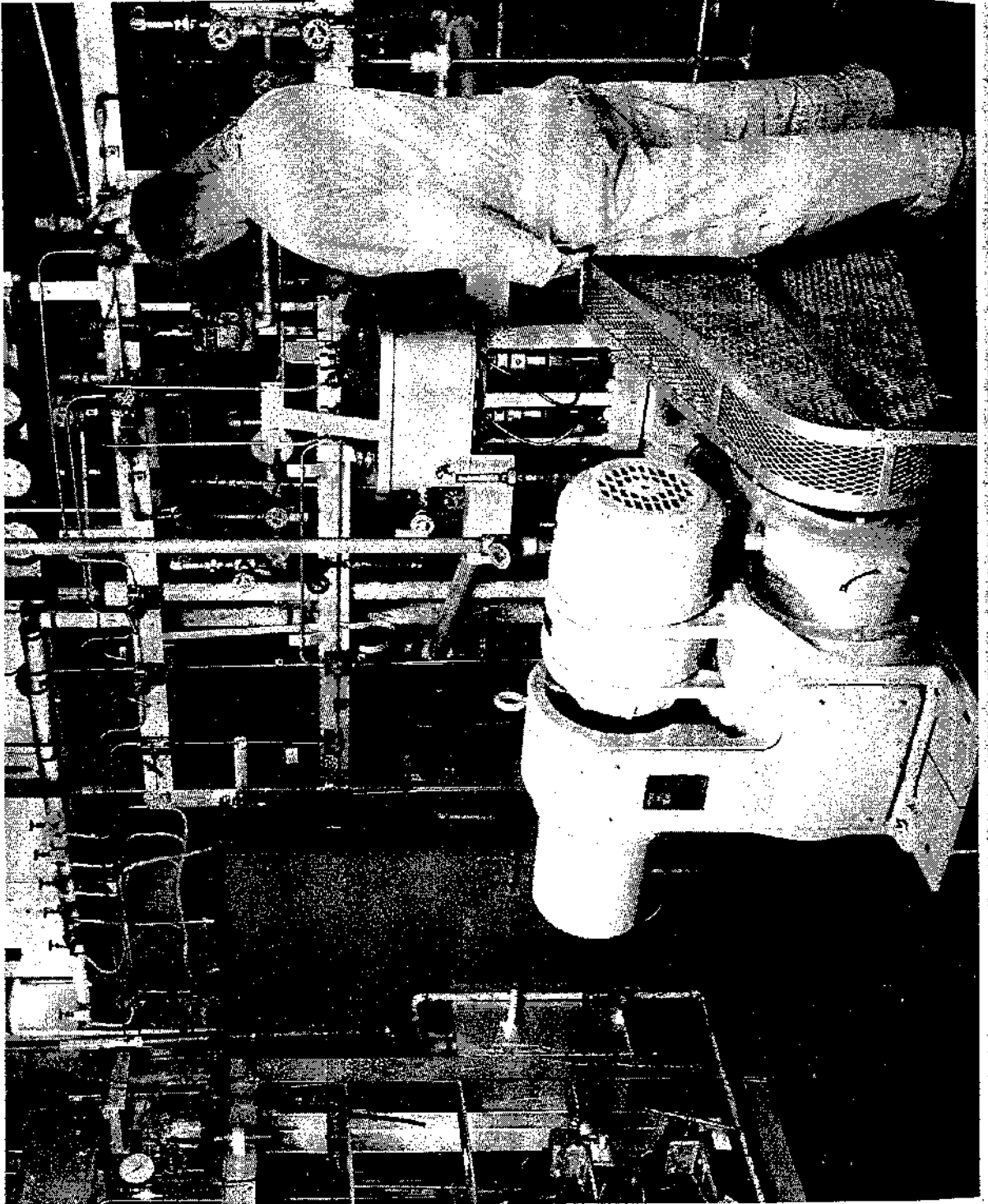


Figure 8- Booster compressor.

studied because the mode of cyclization or polymerization to coallike materials may be followed spectrophotometrically in the presence of dilute acids at low temperatures. The origin of the gases evolved on pyrolysis or acid treatment is being traced with the aid of radioactive sugars.

Experiments on heating and hydrogenation of sugars indicate further the important role of carbonyl. In the first experiments, sucrose was hydrogenated for 1 hour at 400° and 450° C. and an initial hydrogen pressure of 2,500 p.s.i.g. with 1 percent tin plus 0.5 percent ammonium chloride as the catalysts. The products were quite similar to those obtained from hydrogenation of coal. Asphalts and heavy oils from coal and sugar had virtually the same infrared spectra; the heavy oils had virtually the same ultraviolet spectra. Mass, infrared, and ultraviolet spectra for light oil from coal and sugar all were similar. The principal differences were the higher phenolic and slightly higher aromatic content of the coal product.

Hydrogenation of sucrose with copper chromite at 250° C. for 3 hours at 2,500 p.s.i.g. gave only water-soluble, oxygenated compounds. When sucrose was hydrogenated under these conditions or with tin and ammonium chloride, benzene and water-insolubles amounted to about 50 weight-percent of the initial charge. Other products were carbon dioxide, hydrocarbon gases, and water. Identical products were obtained in the presence of ethanol. The residue had an ultimate composition similar to lignite and an infrared spectrum similar to that of anthraxylon. Apparently, copper chromite prevents polymerization and charring of sucrose at 250° C. and catalyzes its hydrogenation to water and alcohols. Furthermore, a sucrose char formed at 250° C. could be hydrogenated at 400° C. with tin and ammonium chloride, with results comparable to those obtained when sucrose is hydrogenated directly at 400° C. with the same catalysts. Hydrogenation of sucrose to oil, water, and gases thus appears to be a two-stage process, coalification or condensation followed by hydrogenolysis of the coalified material.

Arabinose, fructose, sorbitol, and inositol were hydrogenated in the presence of tin chloride for 3 hours at 250° C. and an initial pressure of 2,500 p.s.i.g. Results with the two sugars were virtually identical and similar to those previously obtained with sucrose. Yields amounted to 50 percent char, 9 to 11 percent carbon dioxide, 4 to 5 percent hydrocarbon gases, and 34 to 38 percent water. The infrared spectra of the chars resembled that of coal. Sorbitol yielded only water and oxygenated compounds; inositol did not react.

Infrared Spectra

The infrared spectra of many coal samples have been examined, and several structural assignments have been made in addition to those reported in the literature. Because of interference from minerals in the coal, spectra are usually obtained from anthraxylon instead of whole coal. Bituminous anthraxylons of the same rank from various parts of the world produced the same infrared spectrum; those of different rank produced slightly different spectra. Spectra of coal-hydrogenation asphaltene, petroleum asphalt, and gilsonite were generally similar to coal spectra; the differences indicated quantitative but not qualitative variations in chemical types.

The course of thermal degradation of bituminous anthraxylon was followed by determining spectra after heating at various temperatures. Changes in spectra paralleled the spectral differences between high- and low-volatile bituminous anthraxylons. Bands assigned to aromatic ethers and phenols decreased or disappeared at temperatures below 500° C. Absorption in the visible region of the spectrum extended progressively farther into the infrared region as the temperature was raised. The shift was attributed to an increased number of π -electrons rather than to the formation of condensed polynuclear aromatic systems.

X-Ray Diffraction

The diffraction pattern of Bruceton anthraxylon was analyzed by Fourier analysis and according to Warren's theory of diffraction by a 2-dimensional lattice. Values of interatomic distances in coal were comparable to those in a single graphite layer. The sheet diameter, determined by means of line-broadening measurements, was 13.7 Å.

Riley's method was employed for resolving the gamma band, and its characteristics were compared with those of the diffraction halos of liquid n-heptane and 2,2,4-trimethyl pentane. The average atomic spacing giving rise to the gamma band in coal was found to be almost the same as that in the liquids.

Data obtained by small-angle diffraction were examined for further evidence on whether coal has a "liquid-" or "gas"-type structure. Bruceton anthraxylon was found to have a "gas"-type structure, consisting of particles about 14 Å. in diameter. This value is in good agreement with the size of coal crystallites as determined by line broadening.

Solubility of Polycyclic Compounds in Coal Solvents

A study of solvation of coal by organic solvents should contribute toward elucidating the chemical and physical nature of coal and may reveal a solvent that yields ash-free extracts suitable for studies of coal-hydrogenation. Those solvents which dissolve coal at comparatively low temperatures have been called "specific" as distinguished from solvents effective only at temperatures above 150° C. The most effective specific solvents are compounds which tend to donate a pair of electrons (Lewis bases). Other things being equal, compounds containing nitrogen are more effective coal solvents than oxygen-containing compounds because of their greater tendency to donate the lone pair of electrons. Low-rank coals are more soluble in organic bases than are high-rank coals, because they possess many polar groups, primarily hydroxyl, that promote the solution of macromolecules present in the coal. The number of polar groups is smaller in higher rank coals, and the size of the aromatic lamellae is so large that the coal becomes essentially insoluble in organic bases and other solvents.

The present study is a preliminary attempt to gain information on the mechanism of coal solvation. The solubility of 5 polynuclear compounds in 4 different solvents at room temperature has been investigated. The polynuclear compounds were fluoranthene, pyrene, anthracene, chrysene, and violanthrone; all are hydrocarbons except the last, a dye containing 9 six-membered rings and 2 oxygen atoms per molecule. The solvents were benzene, essentially a neutral compound that is a poor coal solvent; aniline, a weak base with only slight action on coal; pyridine, a weak base with strong solvent action on coal; and ethylenediamine, a strong base and probably the best solvent for coal at room temperature.

Benzene was a poor solvent for all the compounds; ethylenediamine was the poorest solvent for the four polynuclear hydrocarbons. Pyridine, which is almost as effective as ethylenediamine, was the best solvent for fluoranthene, anthracene, and chrysene and a good solvent for pyrene. Although violanthrone contains 9 rings, the presence of 2 oxygen atoms in the molecule was enough to give this compound enhanced solubility in the primary amines studied. There was no doubt, however, that both aniline and ethylenediamine reacted chemically with violanthrone. The solvation of coal by ethylenediamine must be due partly to chemical interaction of the base with oxygenated parts of coal; extracts are known to retain considerable amounts of nitrogen.

Pyridine, which does not react with carbonyl in violanthrone, differs from primary amines because it contains no active hydrogen atoms. Fluoranthene, which has 4 rings, is more than 10 times as soluble in pyridine as anthracene, and similar large differences exist in the solubility of pyrene and the angularly condensed chrysene in pyridine. The high solubility of pyrene in pyridine may indicate the presence of a pyrene-type structure in coal.

Microbial Degradation of Carbonaceous Matter

A microbiology laboratory (see fig. 9) has been established to study the structure of carbonaceous matter (coal and similar sources of liquid fuels) by analysis of products obtained from them by the action of bacteria and other micro-organisms. Bacterial action plays an important role in the formation of carbonaceous residues from plant and animal life. Such bacteriochemical reactions occur on a vast scale at all times. Compared with chemical reactions that often require high temperatures, high pressures, or high concentrations of acids or bases, bacterial reactions are quite mild and, in many instances, highly specific. If such specific reactions can be found for carbonaceous substrates like peat, lignite, or coal, the products of the reactions may be considered to be relatively closely related to the starting materials. The primary purpose of this project is to screen bacteria and other micro-organisms for their reactivity with carbonaceous materials and to use any reactions so discovered for analytical purposes. Better understanding of the structure of peat, lignite, and coal will aid in their conversion to synthetic fuels and chemicals.

The methods (enzyme systems) by which micro-organisms are able to degrade organic matter of high molecular weight without the use of high temperatures or elevated pressures also will be investigated. This work might lead to a process for converting carbonaceous polymers to liquid fuels by microbial action.

Kinetics of Steam-Carbon and Carbon Dioxide-Carbon Reactions at High Temperatures

A large fraction of the total cost of producing synthetic liquid fuels is incurred in gasifying coal to make synthesis gas. One of the fundamental aspects of gasification involves the kinetics of the reactions of carbon with steam and carbon dioxide at high temperatures. The kinetics of the carbon dioxide-carbon reaction has been analyzed, largely on the basis of unpublished data obtained elsewhere, and the problem is nearly solved. The mechanism of the reaction has been determined, and basic kinetic constants have been evaluated. For the first time, carbons of different porosity, crystallinity, and other physical properties have been treated on a common basis. An absolute measure for the reactivity of carbons has not yet been found, although the number of reaction sites alone appears to account for the overall reaction rates of different carbons at 1,300° to 2,550° F. Simplified methods are being developed for evaluation of reactivity.

Analytical Methods

Work has been done on developing an accurate, rapid method for analysis of small quantities of sulfur, organic and inorganic, in Fischer-Tropsch synthesis gases. Gas is passed over a heated platinum spiral that converts sulfur to hydrogen sulfide. Gas is passed over a heated platinum spiral that converts sulfur to hydrogen sulfide which is absorbed and determined by the methylene-blue method. The overall precision of this method is $\pm 1.0 \times 10^{-5}$ grain of sulfur. In the presence of hydrogen, sulfur in thiophene, ethyl mercaptan, diethyl sulfide, and carbonyl sulfide is completely converted to hydrogen sulfide by the spiral at 800° to 1,000° C. An induction or activation period with sulfur-containing gas is required for conditioning the spiral.

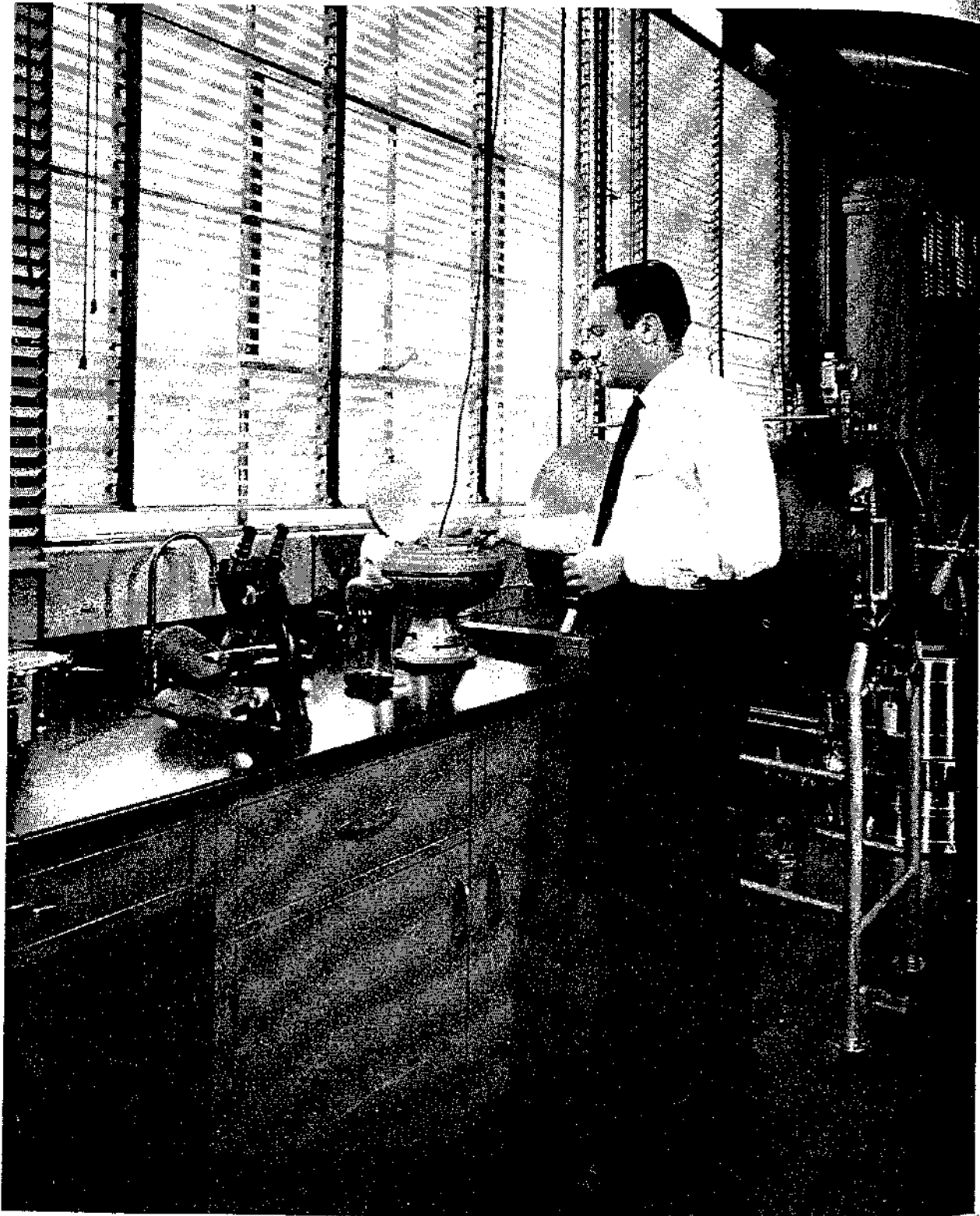


Figure 9. - Part of microbiology laboratory used for studying attack of bacteria on coal and other carbonaceous materials.