

# Synthesis of Liquid Fuels by Hydrogenation of Coal

## High-Temperature Coal Hydrogenation

The objective of the high-temperature coal-hydrogenation program has been development of a one-step process for direct conversion of coal to gasoline. In the process under development the liquid- and vapor-phase stages are combined in one unit operating at temperatures above 500° C. High temperatures, active catalysts, and appropriate throughputs should yield a lower boiling steady-state recycle stock and thus improve the overall yield by minimizing losses of oil during removal of solids. Continuous, bench-scale equipment has been used for the exploratory work. Unfortunately, bench-scale data, obtained on a once-through basis, have little value, and recycle studies appear impractical because the unavoidable losses of liquid represent a large fraction of the total output from such small units.

The major emphasis in pilot-plant development of the high-temperature hydrogenation has been placed upon heat dissipation. Two systems, both employing internal cooling with recycle hydrogen, have been explored. The first system utilized a single vessel for both the preheating and reaction phases. This design was inadequate, in that only a very small portion of the reactor could be maintained at specified temperatures; excessive temperatures occurred in the preheating zone. The second system employed an external preheater and an insulated reactor with internal cooling by hydrogen. This system appears to permit higher rates of heat transfer

and better general operability. With proper instrumentation and operational techniques it was possible to control temperatures at levels ranging from 480° to 520° C. Rock Springs, Wyo., coal was used at a paste rate of 25 pounds per hour and with 8,000 p.s.i.g. hydrogen pressure; however, at the higher temperatures "coke" deposition was noted throughout the reactor.

Bench-scale development concerned catalyzed hydrogenation of vehicle oil at high temperatures and 8,000 p.s.i.g. These experiments were conducted in a 32-foot coil of 1/8-inch inside diameter wound in a helix of 4-inch diameter and immersed in a metallic bath. The temperature of the bath was maintained at 535° C. Feed stock consisted of a 250° to 312° C. coal-hydrogenation middle oil with 0.7 percent molybdenum (based on feed) as powdered ammonium molybdate. Hydrogen rates were varied from 9 to 65 std. cu. ft. per hour, while the feed rate was maintained at 75 grams per hour. Gasoline yields, based on feed, decreased from about 35 percent at the low gas rates to approximately 22 percent at the higher gas rates. These data indicate that virtually all of the gasoline, obtained in past once-through tests with coal-vehicle oil, came from the vehicle oil. Mass spectrometer and ultraviolet analyses of the total product oil showed a naphthalene content of 4 to 9 percent, naphthenes 9 to 13 percent, and paraffins 4 to 5 percent. Benzene and toluene made up about 4 to 5 percent. The refining properties of the catalyst were excellent. The nitrogen, sulfur, and oxygen in the vehicle oil were reduced from the original 0.70, 0.35, and 1.36 percent to 0.00, 0.03, and 0.00 percent, respectively.

Bench-scale studies were also made with coal-oil paste at 8,000 p.s.i.g. and 535° C. to ascertain flow and temperature patterns within the reactant stream and their possible relation to operating difficulties (plugging). Bare thermocouples were placed within the 1/8-inch tube for these experiments. Use of a distillable vehicle apparently contributed to the formation of concentrated coal masses and led to localized carbonization. In the first 10 feet of the 32-foot reactor the internal temperature was below 500° C. Temperatures throughout the remainder of the reactor rose to 800° C. on numerous occasions. Previously, it had been thought that the temperature throughout the reactor was about 535° C., the temperature of the metallic bath.

#### Coal-Hydrogenation Autoclave Studies

The effect of the natural mineral content on the hydrogenation of Rock Springs, Wyo., coal was studied. Comparison was made between washed coal and coal that had been washed and then treated with hydrofluoric and hydrochloric acid to remove more mineral matter. The washed coal contained 4.05 percent ash, and the acid-treated coal 0.87 percent ash. The experiments were conducted in a horizontal, rotary autoclave under 2 sets of operating conditions: 4,000 p.s.i.g. initial hydrogen pressure and 400° C. for 30 minutes; and 3,000 p.s.i.g. initial hydrogen pressure and 500° C. for 15 minutes. With each of the 2 coals and under each set of conditions, 1 test was made with uncatalyzed coal and 1 test each with iron, tin, and molybdenum as catalysts.

When no catalyst was added, the conversion was slightly higher for the coal with the higher mineral content. However, when 1 percent of tin, iron, or molybdenum was added, the effect of original mineral content was entirely obscured, and no difference in yields was observed. As a corollary, the acid treatment of the coal apparently did not affect its hydrogenating characteristics.

A study was made of the effect of alkali on the hydrogenation of coal in the presence of a catalyst. Fifteen-minute tests were made at 2,000 p.s.i.g. initial

hydrogen pressure and 500° and 525° C. The concentration of sodium hydroxide was varied from 0 to 105 weight-percent, based on moisture- and ash-free coal. Within these limits, the concentration of sodium hydroxide had no effect on conversion, which was about maximum in all tests, or on the yields of heavy oil, light oil, or water. As the amount of sodium hydroxide was increased, the yield of asphaltene decreased, and the yield of carbon dioxide increased. Hydrogen consumption, as calculated by an elemental balance, decreased with an increase in sodium hydroxide concentration. This trend indicates that some hydrogen was produced in the overall reaction. The fact that the carbon dioxide contained more oxygen than could have come from the coal supports this reasoning.

#### Hydrocarbonization of Coal

The objective of hydrocarbonization of coal is development of a process for hydrogenating dry coal under conditions that yield either oil or high-B.t.u. gas and a dry char that may be used to produce synthesis gas, hydrogen, or power.

A fluidization technique, which had been tried some years ago at 500 p.s.i.g. and 600° C. on a pilot-plant scale with Rock Springs, Wyo., coal, had resulted in agglomeration of particles in the reactor and consequent loss of fluidization. These studies have been resumed with a bench-scale unit, designed to simulate a pilot-plant system for service at 500 p.s.i.g. and 700° C. The objectives were to determine the effect of particle size, gas velocity, and heating rate upon agglomeration. Results indicate that agglomeration of Rock Springs coal above 400° C. was associated with rapid heating rates, such as are encountered in continuous operation. Free-flowing char was produced at 700° C. by first subjecting the coal to stepwise hydrogenation at 400°, 500°, and 600° C. Char yields decreased from 85 percent at 400° C. to 51 percent at 700° C. Oil yields increased from 3 percent at 400° C. to 19 percent at 600° C. and then decreased to 9 percent at 700° C. Hydrocarbon gas yields increased from less than 1 percent at 400° C. to about 19 percent at 700° C.

#### Structure of Coal

Continuing fundamental studies on the structure and chemistry of coal are supported by Bureau of Mines and cooperative funds. These studies contribute to our knowledge of the origin of coal and help to explain its behavior in chemical reactions. Such knowledge may suggest new possibilities in the development of processes that start with coal as the raw material.

#### Microbial Degradation of Carbonaceous Matter

If microorganisms could be found that use the carbon in peat and coal or coal-like materials, some insight into the structure of coal might be gained by analyzing the intermediate and final degradation products of such action. Further information might also be obtained from studying the microbial dissimilation of pure substances whose structures are similar to portions of the coal structure. Such materials include polycyclic aromatic and hydroaromatic hydrocarbons, and phenolic compounds.

The microflora of North Dakota lignites has been investigated, and various yeasts, molds, and bacteria have been isolated. Certain of the molds grew in an agar-mineral salts medium, with either water-extracted or benzene-extracted lignite added as a source of carbon. Growth of a Penicillium sp. was noted also on extracted lignites in a liquid medium containing peptone and on material extracted from lignite with water.

Cultures, mostly species of Pseudomonas, from oil-soaked soils were apparently able to utilize chrysene and light-oil bottoms (boiling above 325° C.) from a Louisiana coal-hydrogenation oil when these materials were supplied as carbon sources in mineral media. Enrichments with middle oil (boiling range, 260° to 325° C.) from the Louisiana, Mo., coal-hydrogenation plant have yielded no growth of microorganisms. Growth curves obtained from the light-oil bottoms indicate that the mixed flora attack 1 component of the oil at a time, first attacking 1, lagging, then adapting to another. Such cyclic fermentations are not uncommon in bacterial attack of nonhomogeneous substrates.

#### Formation of Bituminous Materials

This work is concerned first with the information that can be obtained by correlating the structure of various compounds with that of the bituminous substances formed on pyrolysis, and second with the mode of formation of bituminous substances from known substances. Compounds that form bituminous materials on pyrolysis have fairly specific structural groupings. From a knowledge of these specific and necessary structural units in the starting material and of the fairly limited ways in which these units can react, clearer understanding of the structure of coal is being obtained. Char formation was studied because of the assumption that it is a prerequisite to coalification and the formation of bituminous materials.

Pyrolyses of organic substances were conducted at 300° and at 400° C. A definite relationship was found to exist between the structure of the starting material and char formation at 300° C., although none of the 300° C. chars had infrared spectra resembling that of coal. A char was considered coallike if it met the following criteria: An ultimate composition within the coal range; insolubility in benzene, ethanol, acetone, and the usual organic solvents; and an infrared spectrum closely resembling that of coal.

Substances that have a hydroxyl group on every carbon and also a carbonyl group or an incipient carbonyl group (glucose, sucrose, fructose, etc.), yield chars at 300° C. When the carbonyl group is hydrogenated to an alcohol group (that is, sorbitol, glycerol), no char is formed. A molecule need not have six carbons to yield the aromatic structure found in the chars, since arabinose (5 carbons) and glyceraldehyde and dihydroxyacetone (3 carbons each) yield coallike chars.

Chars are formed only from starting materials that can yield reactive intermediates at essentially every carbon atom in the chain. Chars are formed by condensation reactions involving ionic or radical intermediates that result from dehydration or cyclization. The most probable intermediate is a carbonium ion formed in the process of dehydration.

Substances (such as furfural) that have at least one carbonyl group and a conjugated carbon chain but that cannot form these intermediate fragments do not yield bituminous substances. Substances (such as vanillin) that have a carbonyl group and a conjugated carbon chain plus 1 or 2 reactive hydroxyl or other groups form chars that are not coallike because the number of potential intermediates is too small. Two compounds that partly exemplify this point are coumarin and 5,7-dihydroxycoumarin. Both have the basic coumarin structure. Although coumarin itself is too unreactive to form a char, the addition of two hydroxyl groups furnishes sufficient points of activity so that dihydroxycoumarin does char, although this char does not have a coallike infrared spectrum. A bituminous material resembling coal might be formed from a coumarin with three or more hydroxyl groups. Somewhere between the carbohydrate molecule (glucose) and the completely dehydrated molecule (furfural), the

ability to form a char is lost; a possible explanation is that this property disappears when the intermediate substances become too stable.

Work with labeled glucose has shown that the gas formed on pyrolysis comes mostly from C<sub>1</sub> (the carbonyl group) and C<sub>2</sub>. However, some gas probably originates from each of the other carbons.

#### A New Reducing System for Organic Compounds: Lithium in Ethylenediamine

A new method has been found for hydrogenating organic compounds and splitting linkages at low temperatures. It consists of adding lithium to a solution of the compound in ethylenediamine at 80° to 110° C. The lithium-ethylenediamine system is experimentally much more convenient and versatile than the sodium-liquid ammonia or lithium-ethylamine systems. Furthermore, the lithium-ethylenediamine system appears to be the most powerful metal-amine reducing system known. Terminal and internal double bonds, aromatic rings, polynuclear hydrocarbons, ketones, phenols, and ethers are either reduced or cleaved by this new method. This is the first method known of reducing phenol chemically and the first instance of cleavage of an aliphatic ether in a metal-amine system. The reaction is being extended to the reduction of lignin, peat, coal, and oils derived from coal.

The reductions and cleavages which have been carried out with lithium in ethylenediamine may be summarized as follows:

<u>Substrate</u>	<u>Products</u>
Benzene	Cyclohexene and cyclohexane
Tetralin	$\Delta^9$ -Octalin $\rightarrow$ trans-decahydronaphthalene
Phenanthrene	Tetrahydro- and octahydrophenanthrenes
Anthracene	Dodecahydro- and tetradecahydroanthracenes
Phenol	Cyclohexanone and cyclohexanol
Anisole	Phenol, $\Delta^2$ -cyclohexenone, cyclohexanone, cyclohexanol, cyclohexene, and cyclohexane.
Heptene-1	Heptane and heptene-2 or -3
Di-n-hexyl ether	Hexanol and hexene-2 or -3
Heptanone-3	Heptanol-3
Benzyl alcohol	Hexahydrobenzyl alcohol

#### Determination of Optical Activity in Coal-Hydrogenation Oils

Petroleum is known to be optically active. This fact and the knowledge that coal must have originated from biological materials that were highly active optically has prompted an investigation into the possible optical activity of coal-hydrogenation products and coal-carbonization products.

Examination of a vehicle-oil after initial distillation showed that optically active substances were indeed present. As far as could be ascertained, this is the first discovery of optical activity in an oil derived from coal.

The coal-hydrogenation oil was fractionated by extraction with alkali, distillation, and finally chromatographic separation. The tar-acid fraction and the aromatic and polar portions of the neutral-oil were optically inactive. The active portion was further concentrated by formation of urea adducts. Characterization of the fractions of highest optical activity suggest that they contain naphthenic, dinaphthenic, and paraffinic compounds with an average molecular weight of about 200. This research may provide clues regarding the structure of coal and reactions that occur in the production of oil from coal.

### X-ray Diffraction Studies on Coal

Several coals, sugar chars, and benzene-insoluble residues from coal hydrogenation runs were studied by X-ray diffraction. A 57.3-millimeter evacuated Debye-Scherrer camera was used (see fig. 5).

Coal appears to consist of platelets of catacondensed aromatic nuclei, together with a highly amorphous constituent that scatters X-rays as though it consisted of essentially isolated atoms of carbon. The diffraction patterns of most coals are accounted for by this model. Some coals, particularly the sapropelic and boghead coals, contain a large amount of another constituent that appears to be a highly viscous, mainly aliphatic liquid. This material, which can be identified by a broad band corresponding to the Bragg spacing of about 4.6 angstroms, has a diffraction pattern similar to that of the asphaltene fraction obtained in coal hydrogenation.

Search has been made for a material with coallike chemical characteristics that has a diffraction pattern similar to that of bituminous coal. Sugar charred in vacuo at 400° C. yields a char that fulfills these conditions. The char and the coal have similar diffraction patterns and infrared spectra. On hydrogenation, both yield the same products. The ash-free char may thus be useful as a coal "model" for studying chemical behavior in the absence of mineral material.

Benzene-insoluble residues from coal-hydrogenation autoclave runs have been examined by diffraction methods. Preliminary results show that the residues from mild hydrogenation are coallike and that the stacks of platelets are somewhat higher than in the original coal.

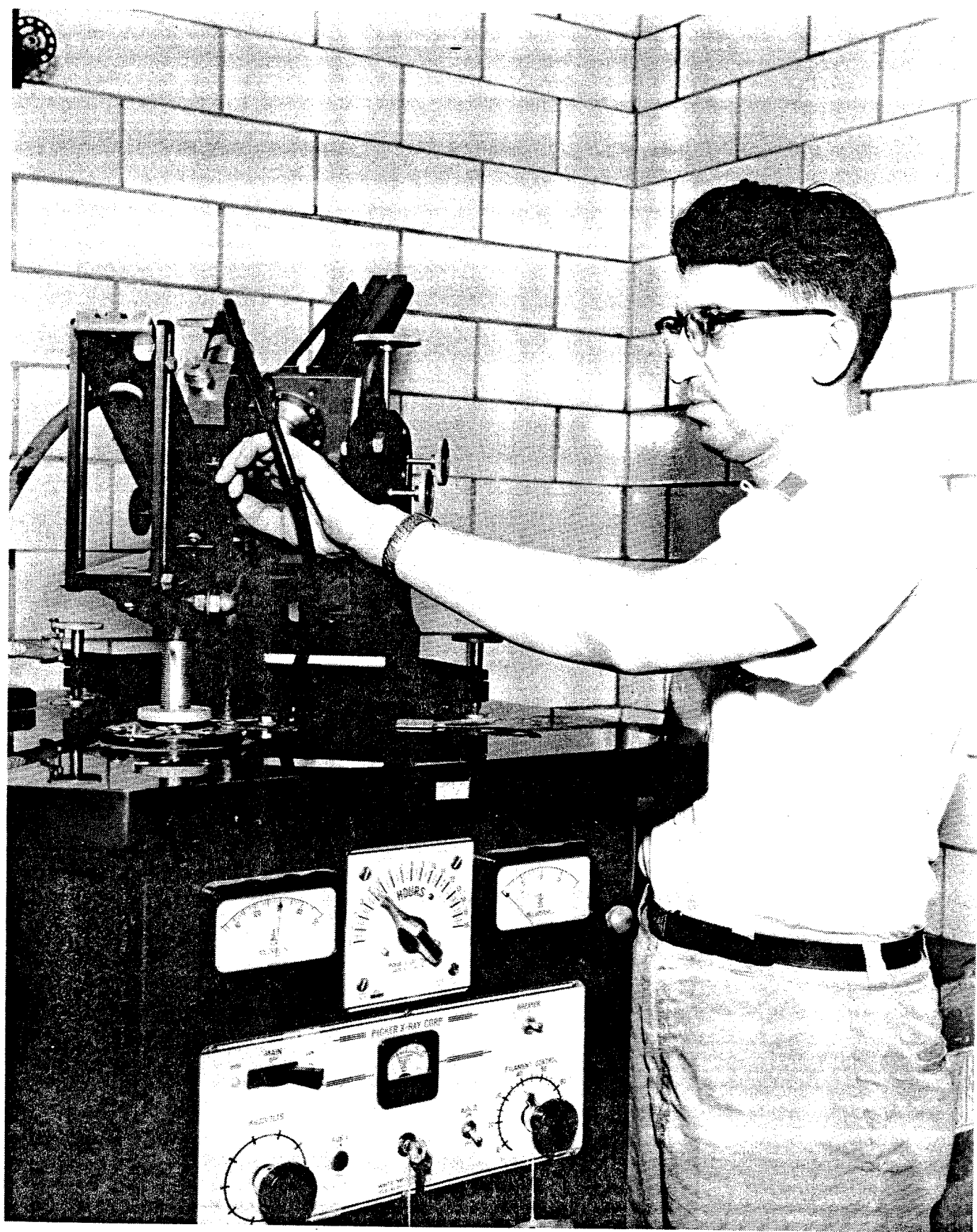


Figure 5. - Debye-Scherrer vacuum X-ray camera.

## COAL-TO-GAS LABORATORIES AND PILOT PLANTS, MORGANTOWN, W. VA.

The cost of synthesis gas, essentially carbon monoxide and hydrogen, is 50 to 80 percent of the cost of gasoline, alcohol, ammonia, pipeline gas, and other such products made from coal. The object of the work of the Morgantown, W. Va., station has been to develop lower cost processes for gasifying coal. Until early in 1955 the approach was to react oxygen and steam with pulverized coal, at first at atmospheric pressure and later at high pressure. Laboratory work is now in progress to develop gasification by nuclear energy. Research is being conducted also on producing oxygen by methods other than liquefaction of air.

Work on gasifying powdered coal with oxygen and steam at atmospheric pressure terminated in 1954 with demonstration of a practical process. At that time a large-scale commercial plant, using such a process, was built in West Virginia. Accordingly, the atmospheric-pressure pilot plant has not been reerected at the new station.

Pilot-plant-scale investigation of coal gasification at high pressure (about 30 atmospheres) is continuing. The high-pressure pilot plant and all auxiliary services have been installed at the new station (fig. 6). Auxiliary facilities have been installed for preparing coal, for feeding coal pneumatically to the high-pressure gasifier (see fig. 7), for feeding coal-water slurries, for supplying steam at pressures up to 600 p.s.i.g. and 1,000° F. (see fig. 8), and for compressing gases.

With the move to the new Appalachian Experiment Station, no new pilot-plant work was possible during the latter half of the calendar year 1954 and the first 5 months of 1955. However, data from previous experiments, in both the atmospheric-pressure and the high-pressure pilot plants, have been evaluated, and detailed reports of this work are being prepared. The results for the atmospheric-pressure plants are discussed below.

### Results With Atmospheric-Pressure Gasifier

Equipment and methods were described in the 1954 and earlier reports. As used in this work, the atmospheric-pressure gasifier contained a silicon carbide refractory lining in the primary-reaction zone. This lining was backed by water-cooled coils and gave very good service.

Tests were carried out on three coals: Lake deSmet, a subbituminous C coal from Wyoming; Sewickley-bed, a bituminous coal from West Virginia; and a Pennsylvania anthracite. These tests were conducted in three series of factorial experiments. Variables were: Oxygen/carbon ratios of 10.5, 12.5, and 14.5 std. cu. ft. per pound; steam/carbon ratios of 0.35, 0.70, and 1.0 pound per pound; and carbon-input rates equivalent to coal rates of 400, 600, and 800 pounds per hour of the bituminous coal.

The results of the tests were studied by covariance analysis. This analysis of the data indicated that, at the same oxygen/carbon ratio, gasification was highest and materials requirements were lowest for the lowest rank subbituminous coal. The heat loss was highest for anthracite and lowest for Lake deSmet coal, in line with the higher reaction temperature of anthracite.

Gasification of Sewickley-bed bituminous coal increased and contact time decreased with increasing rates of coal throughput, but the heat loss per cubic foot of synthesis gas decreased because the rate of total heat loss was essentially constant. Similarly, oxygen and coal requirements decreased, the percentage of CO<sub>2</sub> decreased, and the percentage of CO + H<sub>2</sub> increased as the coal rate was increased.



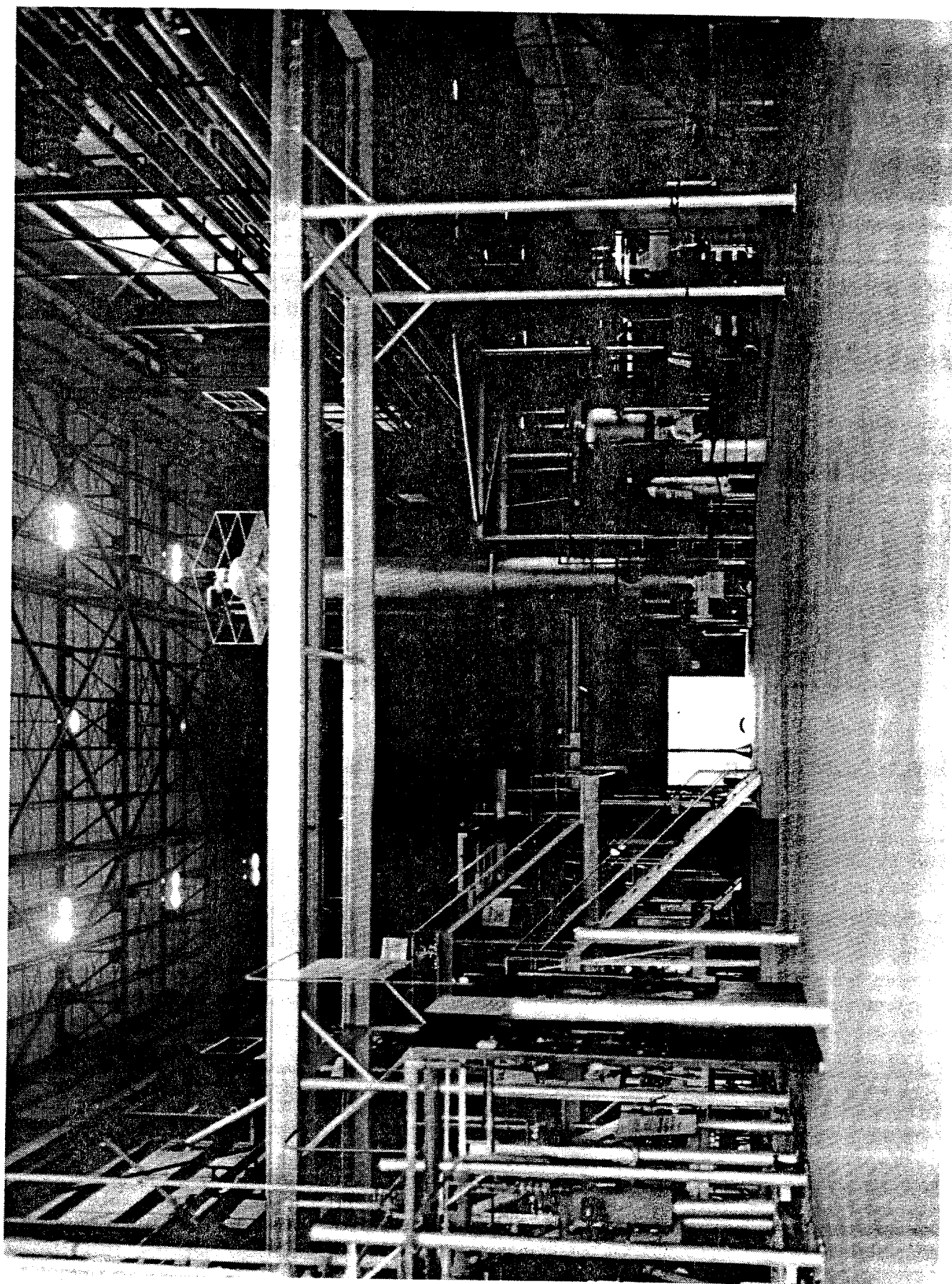


Figure 6. - Comprehensive view of gasification pilot plant.

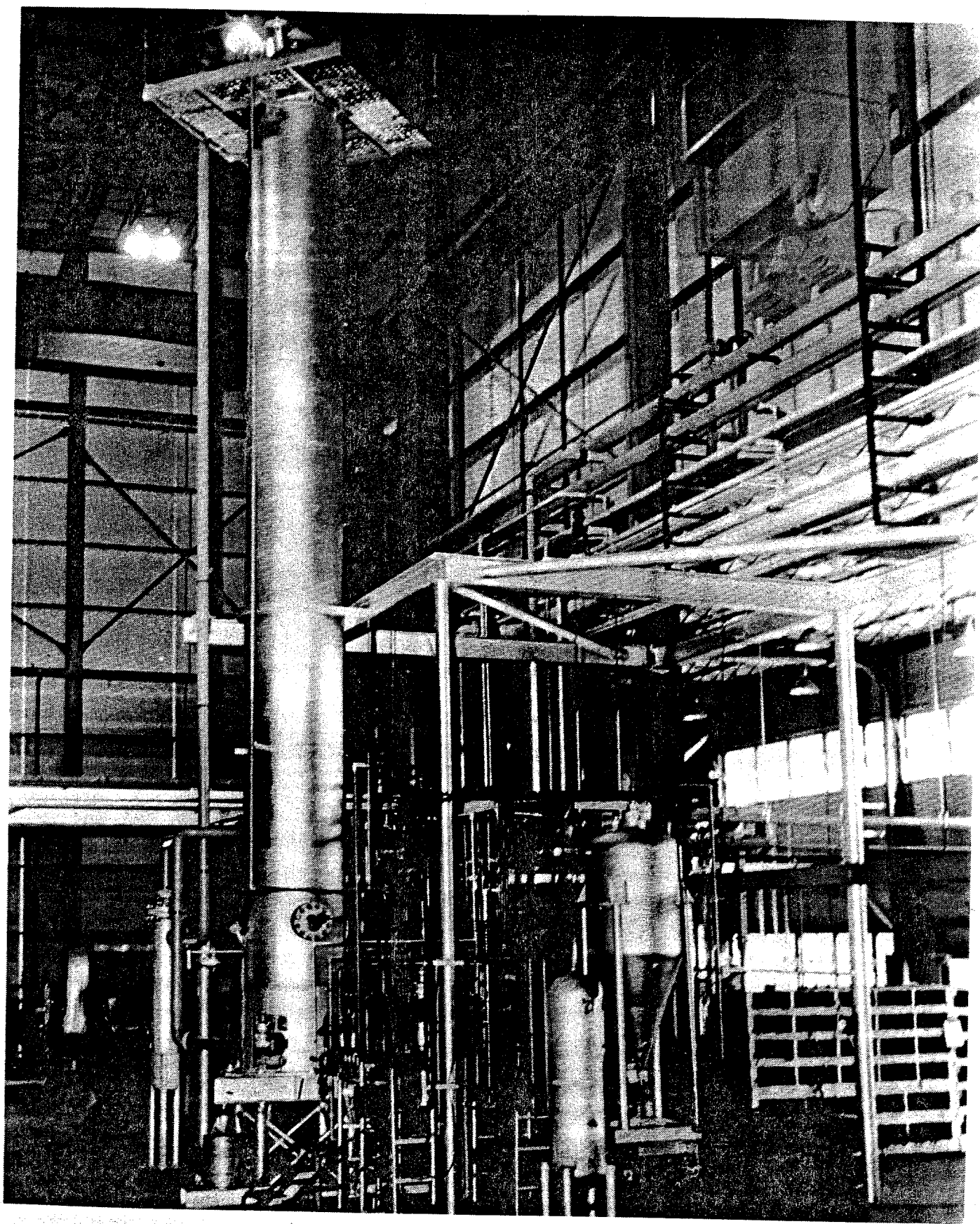


Figure 7. - Pneumatic coal feeder and related equipment in pilot plant.

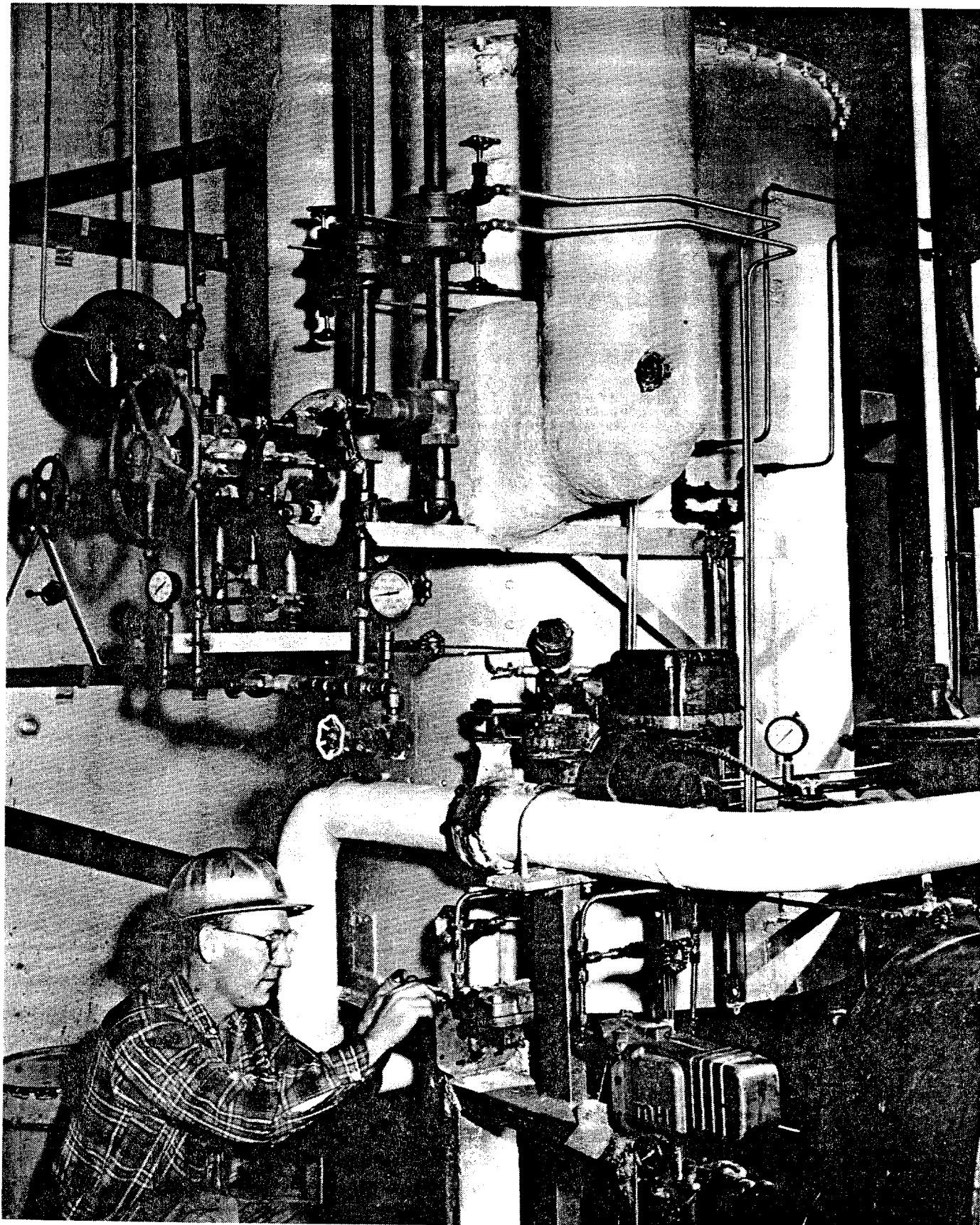


Figure 8. - Boiler superheater that furnishes steam for gasification experiments.