

Bureau of Mines
Report of Investigations 4865



SYNTHETIC LIQUID FUELS

ANNUAL REPORT OF THE SECRETARY
OF THE INTERIOR FOR 1951

PART I. - OIL FROM COAL

United States Department of the Interior— July 1952

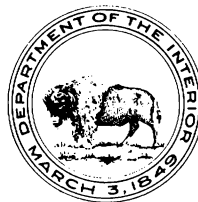
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UNITED STATES DEPARTMENT OF THE INTERIOR
Oscar L. Chapman, Secretary
BUREAU OF MINES
J. J. Forbes, Director

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July 1952

SYNTHETIC LIQUID FUELS

Annual Report of the Secretary of the Interior for 1951

Part 1. - Oil from Coal

PREFACE

This report is submitted in accordance with the provisions of the Synthetic Liquid Fuels Act of April 5, 1944 (30 U.S.C. 321-325, as amended), which require that: "The Secretary of the Interior shall render to Congress on or before the first day of January of each year a report on all operations under this Act."

Owing to the broad scope of the content and the diversity of interests represented, the Annual Report for 1951 has been divided into two separate publications. Each has been published by the Bureau of Mines as a Report of Investigations, and the respective titles follow:

R. I. 4865, Part I - Oil from Coal.

R. I. 4866, Part II - Oil from Oil Shale.

Identical in each report, the introduction summarizes research progress made in 1951 under the entire Synthetic Liquid Fuels program.

A free copy of these publications may be obtained by a written request to the Bureau of Mines, Publications Distribution Section, 4800 Forbes Street, Pittsburgh 13, Pa. The R. I. number and title of the publication desired should be indicated.

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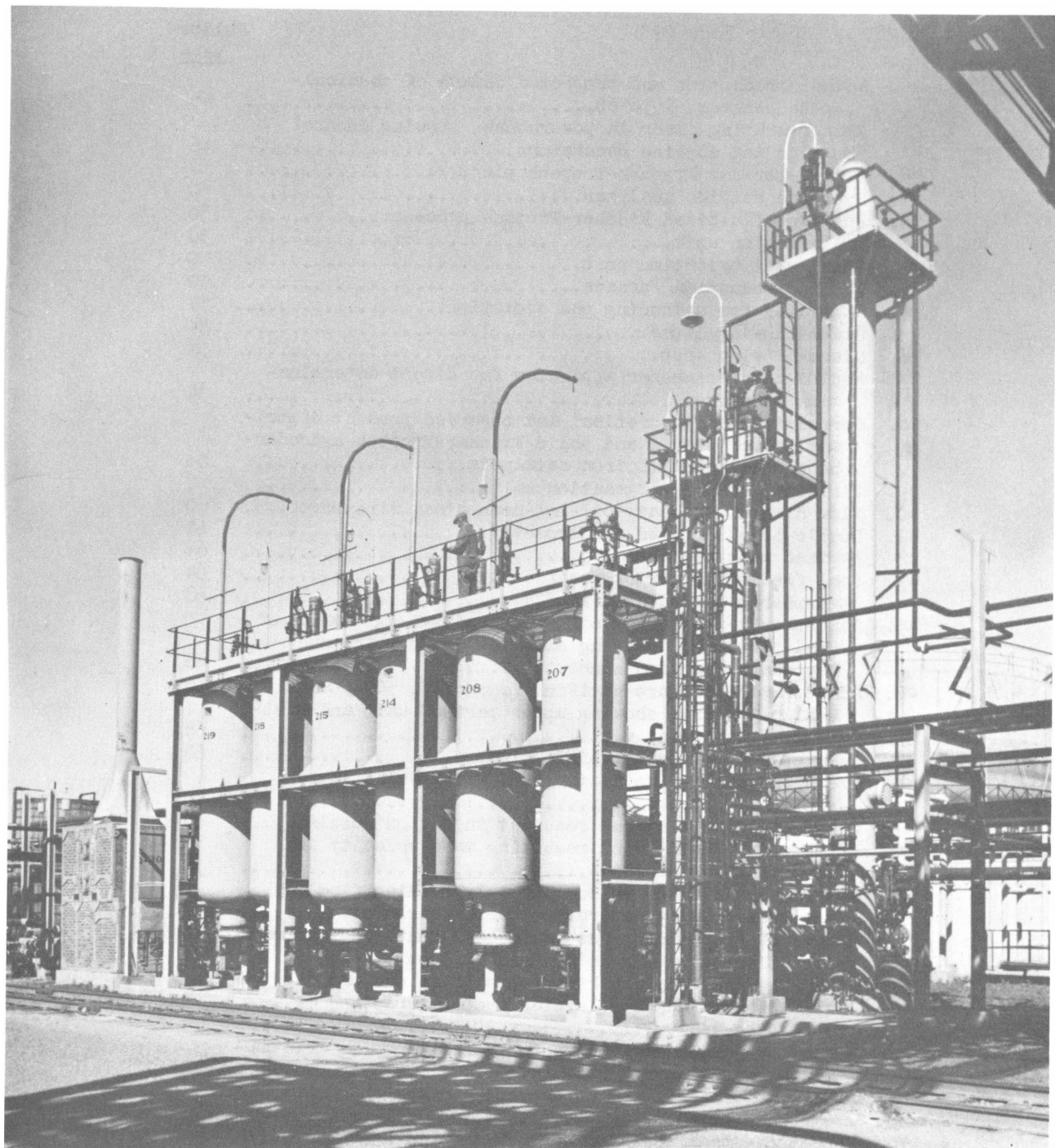


Figure 1. - Gas-purification unit of new Gas-Synthesis Demonstration Plant, Louisiana, Mo. Here harmful sulfur compounds and carbon dioxide, obtained in gasifying raw coal, are removed from compressed synthesis gas before it is fed to reactor for conversion into synthetic oil.

INTRODUCTION

Increasing demands for liquid fuels and the critical state of world affairs emphasize the importance of the Bureau of Mines synthetic liquid fuels program.

Before World War II, the United States produced all the oil necessary to meet domestic demands and, in addition, had a comfortable excess production that was used to supply a large portion of the world's needs. Soon after the war, however, domestic demands increased sharply, placing a severe burden on America's oil resources. No longer was this country able to export large quantities of oil; in fact, foreign oil was imported in increasing quantities. In spite of an increase in exploration and drilling activities, imports continued to rise; and last year, over 10 percent of the total demand was met with foreign oil.

There is strong evidence that dependence on foreign oil will continue to increase and sooner or later may create a security problem. Although it is impossible to prove that this will occur, the mere possibility of a security problem with a material as essential as oil makes it imperative to develop all possible new sources of domestic oil.

The fact that the United States is now in a position to design and construct pioneer synthetic fuels plants is a tribute to the cooperative efforts of American industry and Government. It will be remembered that in 1944, when the Bureau of Mines synthetic liquid fuels program got underway, there was no production of synthetic fuels in the United States, and the technical information available was meager indeed.

As a result of the Bureau of Mines program and the increased activity of private industry, significant progress has been made during the past 7 years. One commercial synthetic fuels plant using natural gas has been constructed; oil-shale processes are nearing commercial exploitation; coal hydrogenation has been demonstrated with American-built equipment and commercial plants have been proposed; in 1951 the Bureau successfully demonstrated a new gas-synthesis process; and significant advances have been made in developing direct coal-gasification processes.

The Bureau of Mines and the National Petroleum Council have cooperated in making studies of operating costs for coal hydrogenation and oil-shale retorting. Both the Bureau and industry have benefited by the results of this

cooperative effort. The Bureau and the N.P.C. have been in good agreement on many points in these cost estimates. On some items there has been wide divergence, and it is believed advisable to continue the studies.

Oil Shale Ready for Exploitation

Some of the most outstanding achievements have been in the oil-shale phase of the program. While initially, oil shale seemingly offered only a slight promise of success, today, it generally is considered to be the most promising large-scale source of synthetic liquid fuels.

Progress in Shale Technology

Great strides have been made in all phases of the oil-shale development program, from mining the shale and extracting the crude oil to refining the oil into finished products.

One of the important developments has been the demonstration of practical methods for mining oil shale underground at the very low cost of approximately 50 cents per ton. When this cost figure was set as a goal at the outset of the mining research program, few technical experts expected that it would be reached. It was reached, however, despite an inflationary trend that has nearly doubled costs of labor and material since the work was started.

Considerable progress also has been made in retorting shale. Only 7 years ago no economical retorting process was known that was suitable for American shales. It was a question of determining the fundamental principles involved and learning how best to apply them. Today, two economical retorting processes are available. Both have been developed through the pilot-plant stage, one by the Bureau of Mines and one by the petroleum industry. Each retort is a rugged, one-vessel unit tailored to fit the particular conditions of the oil-shale regions. Neither process requires cooling water, and both provide highly efficient, continuous operation.

At the start of the synthetic fuels program, refining the crude shale oil posed numerous problems, some of which appeared to be almost insurmountable. The general opinion was that high-grade products could be made from crude shale oil only under the most severe operating conditions and at very high costs. However, concerted development efforts since have produced several suitable refining processes which yield high-grade products and yet operate at moderate conditions and reasonable cost.

Shale-oil products are used regularly in the Bureau's motor cars and Diesel trucks and perform entirely satisfactorily. Likewise, large-scale tests in Diesel locomotives have proved shale-oil Diesel fuel to be wholly suited for this use.

Shale Economics Are Good

By virtue of these technical advances in mining, retorting, and refining, oil shale now occupies a very interesting economic position. The Bureau estimates that, with a capitalization of 50 percent equity and 50 percent borrowed

funds and with all products selling at market values, the rate of return on the equity capital would be 11.2 percent after interest charges and income taxes. This return is based on an industry-scale operation and includes the cost of a pipeline to the west coast. Although this return is less than the average return of the petroleum industry, as indicated by published figures, it is high enough to warrant serious attention. Furthermore, oil-shale operations would not involve the exploration risks incident to crude-oil production.

Shale Requires Less Steel Than Petroleum

An industry-scale oil-shale operation, including a pipeline to the west coast, as well as all plant facilities, would require about 3 tons of construction steel per barrel of product. This means that substantially less steel is required to produce fuels from oil shale than to establish new fuels production from petroleum, including exploration and drilling. The fact that oil shale could be utilized to expand liquid fuels production with actual savings in steel is particularly significant now, when the foreign situation is unstable and the defense program is placing a heavy drain on our steel supplies.

Construction of Prototype Plant Encouraged

Sooner or later this Nation will rely in part on synthetic liquid fuels, and from the standpoint of security it is essential that it be fully prepared when the time comes.

The Department of the Interior believes that it would be prudent for private industry to establish a pioneer commercial oil-shale plant. The vast oil-shale resources, lying as they do within our own borders, assure a steady flow of oil in almost any emergency. Such a plant would prove the potentialities of America's oil shale resources and would justify increasing present estimates of proved oil reserves by many billions of barrels.

New Gas-Synthesis Process Developed for Oil-from-Coal

The progress made in developing methods for converting coal into liquid fuels parallels that for oil shale.

The gas-synthesis process, by which gas from coal, consisting of hydrogen and carbon monoxide, is converted into liquid fuels, was used commercially by the Germans. However, their plants left much to be desired. Sweeping technical improvements were necessary before the process could be considered for use in this country, because the German reactors required large quantities of steel and were very expensive. Furthermore, the largest reactor they used had a capacity of only 20 barrels a day, which meant that a commercial plant of several thousand barrels capacity would require a multitude of reactors with attendant high requirements of manpower and materials.

Opinion in the Bureau held that successful development of an acceptable gas-synthesis process depended on finding an efficient, rapid method of removing the tremendous quantities of heat evolved in the reaction. If this problem could be solved, permissible throughputs would be increased greatly; and as a result, material and manpower requirements would be reduced.

Approaching the problem with this in mind, the Bureau began experimenting on a small scale in its research laboratories at Bruceton, Pa. Rather than attempt to remove the heat from the reaction indirectly, as the Germans had done, the Bureau decided to dissipate the high heat of reaction directly by circulating cooling oil through the catalyst bed. Numerous problems were encountered in the initial experiments, and early results were discouraging. When experiments in the small, bench-scale equipment proved that the heat could be removed by this method, larger pilot plants of a 3-gallon-a-day capacity were built. Finally, successful development of a new process depended on the solution of one major problem. After the converter had been operated briefly, the bed of catalyst particles became cemented together, the circulating oil could not remove the heat generated, and, as a result, throughputs fell off sharply.

This difficulty was overcome by speeding the flow of cooling oil enough to keep the individual particles in constant motion, thereby preventing the bed from cementing together.

Upon gaining the necessary experience on the smaller pilot plants, the Bureau next constructed a larger 1-barrel-a-day pilot plant at Bruceton. This plant operated very satisfactorily and substantiated the previous development work.

Design and construction of a 50-barrel-a-day demonstration plant at Louisiana, Mo., were undertaken as rapidly as possible, and the plant was completed during the summer of 1951. A shake-down run was started on September 12; and, after necessary minor revisions were made, a comprehensive test run was started on October 23. This run, lasting 25 days, was entirely satisfactory. Some 75 to 85 percent of the synthesis gas was converted to liquid products in a single pass at a throughput six times greater than that attained in German reactors, and substantial quantities of gasoline and Diesel fuel were made.

High-Pressure Coal Gasification Advancing

Progress has been made toward developing an economical process for gasifying coal to make synthesis gas for the Fischer-Tropsch conversion and for generating hydrogen for direct hydrogenation of coal.

The latest and most important development is the gasification of powdered coal under pressure. A 500-pound-per-hour pulverized-coal gasifier using steam and oxygen and designed to operate at a pressure of 450 pounds has been constructed. Preliminary runs at 100 pounds pressure have been successful, and operating pressures are being increased gradually.

In addition to being the basic process for coal-to-oil operations, gasification also is the key to economical production of fertilizers from coal. The development of an inexpensive coal-gasification process very probably would open the door for large-scale fertilizer operations using coal as the raw material.

Commercial Gas-Synthesis Plants

After analyzing the progress that has been made, it is evident that the information necessary for designing commercial gas-synthesis plants starting with coal will be available soon. Demonstration of a high-pressure coal gasification process is the most important problem remaining. A low-cost gasification process would make an important contribution toward economical production of liquid fuels from coal by the gas-synthesis process.

American Equipment Used Successfully in Coal Hydrogenation

Coal hydrogenation, which involves direct reaction of coal with hydrogen to produce liquid fuels, already was a proved process when the Bureau's synthetic liquid fuels program was started, as the Germans had used it to produce virtually all of their aviation gasoline for World War II. However, coal hydrogenation was not in use in the United States; and, because the process operates at higher pressures than ordinary fuels plants, much of the specialized equipment had never been made in this country.

Probably the greatest achievement in coal hydrogenation has been the design and fabrication of new, and in many instances, improved equipment by American industry, and the use of this equipment in building and operating the Bureau of Mines Demonstration Plant at Louisiana, Mo. Although it would have been much easier to obtain the highly specialized equipment from Germany, it was decided to build a completely American plant. This required the cooperation of numerous manufacturers. As a result, industrial concerns are now in a position to supply such equipment. Improvements over German plants, especially in instrumentation and control, have been incorporated in the 200-to-300-barrel-per-day demonstration plant at Louisiana. Four American coals have been successfully processed in the plant, and the gasoline produced has been extensively tested by the Armed Forces and found to be very satisfactory.

Coal-Hydrogenation Cost Estimates

Bureau of Mines estimates for coal-hydrogenation production costs for two assumed locations, Rock Springs, Wyo., and western Kentucky, were completed during the year. The Bureau contracted with Ebasco Services, Inc., a prominent engineering, management, and consulting firm, to make an independent review of some of the more important costs included in these estimates.

Ebasco's evaluation included a detailed study of two important items of construction costs; an extensive analysis of six major operating cost factors; a comprehensive study of the marketability of chemical coproducts; and an investigation of company-financed housing requirements. Ebasco also studied methods of financing initial plants.

The Ebasco studies supported many of the important cost factors previously estimated by the Bureau. Following is a comparison of some of the factors estimated by Ebasco and the Bureau for an assumed plant at Rock Springs, Wyo., based on January 1951 conditions:

Comparison of cost estimates for a coal-hydrogenation plant
at Rock Springs, Wyo.

(All figures are based on conditions as of January 1951)

	<u>Bureau</u>	<u>Ebasco</u>
Plant-capacity basis - barrels per calendar day	30,000	30,000
Power plant	\$55,500,000	\$51,400,000
Hydrogen compression and purification facilities ...	57,948,000	56,184,000
Company-financed housing and community facilities ..	5,000,000	250,000
Percent equity capital	40	50

Other important comparisons have been developed by adjusting the Bureau's figures to take account of the Ebasco findings as follows:

	<u>Bureau original</u>	<u>Bureau figures revised to include Ebasco findings</u>
Total capital investment	\$414,440,000	\$403,827,000
Annual production costs including depreciation	53,199,500	58,753,500
Annual value of fuels and chemicals, includ- ing gasoline at 11 cents per gallon	79,859,000	76,180,700
Average return on equity capital with gaso- line at 11 cents per gallon	6.98 percent	3.59 percent
Production costs (before net income, inter- est charges and income taxes), per gallon of total product	1/10.2 cents	1/11.4 cents
<u>1/</u> After credits of \$6,254,000 income from sale of ammonium sulfate and sulfur.		

It should be emphasized that the Ebasco evaluations represent its best judgment, based on independent studies. Ebasco obtained information from a wide variety of sources, including discussions on housing with individuals at the sites; information on equipment costs from industry; information from railroads and other agencies in product handling; information from the chemical industry and defense agencies on chemical demands; and information on manpower requirements from specialized industries, such as synthetic ammonia, petroleum refining, and others.

As indicated in the foregoing table, Ebasco's independent estimates for the power-plant and hydrogen compression and purification facilities, which account for about 25 percent of the total investment, were lower than the Bureau previously estimated. In its report Ebasco stated that these estimates, "constitute a close check of the Bureau's figures for these facilities and in effect confirm the original estimates and the accuracy of adjustments made by the Bureau."

In the matter of company-financed housing, previous Bureau studies had indicated that no provision for community facilities or employee housing would have to be included in the capital requirements of a coal-hydrogenation plant at Rock Springs, Wyo. However, the Bureau estimates did include an item of

\$5,000,000 to assist the surrounding communities in providing the necessary facilities. After careful examination of all the factors involved, Ebasco concluded that existing communities near the plant site would be willing to provide the necessary facilities and that only \$250,000 need be included in the capital requirements to assist local planning groups and to protect the interests of the plant and its employees.

To insure an accurate appraisal of operating costs, the Bureau requested Ebasco to draw up complete manpower tables, including maintenance and operating labor as well as administrative, supervisory and clerical help, and to base related operating costs on these manning tables. Ebasco's findings on these items raised the Bureau's estimates of over-all operating costs by 10 percent.

It is of interest to compare actual production costs, before net income, interest charges, and income taxes, per gallon of total product because the nontechnical factors of financial arrangements and income taxes on which there is a greater variation of opinion are not involved. On this basis, the Ebasco findings increased the Bureau's previous estimate of 10.2 cents per gallon of total product to 11.4 cents, after credits for the sale of ammonium sulfate and sulfur.

Based on chemical market surveys, the Bureau, in its previous estimates, took advantage of the versatility of the coal-hydrogenation process to produce aromatic hydrocarbons and other chemicals as well as fuels. Production of these materials improves the economics of the operation because they can be readily sold at prices much higher than motor fuel. The Bureau also included facilities for producing ammonium sulfate and sulfur from the waste streams.

Ebasco made a thorough study of the chemical market potentials over the next several years and, with only one exception - namely, m-p-cresol - concurred with the Bureau's estimates of the marketability of chemicals from a single plant.

It is apparent, from the factors discussed, that the independent evaluation of Ebasco lends considerable support to the correctness of the Bureau's coal-hydrogenation cost estimates.

It must be emphasized that all of the estimates compared are for a so-called conventional plant the design of which is more or less frozen as of January 1951 and does not include important improvements that now are considered feasible as a result of the Bureau's technical studies on coal hydrogenation. These improvements, combined with additional facilities for producing greater quantities of valuable chemicals, would make the first commercial plants more attractive investments.

The Bureau of Mines is now proceeding with detailed studies of a modernized plant, including recent technical improvements and facilities for increased production of chemicals to determine coal-hydrogenation economics under these more favorable conditions.

Steel Requirements for Coal Hydro Not Excessive

There is a widespread impression that steel requirements for coal hydrogenation are excessively high. Actually, on an equivalent product basis, coal hydrogenation requires about the same amount of steel per daily barrel of product as the petroleum industry, including exploration and drilling. Coal hydrogenation yields higher-grade products than those normally obtained from petroleum. For example, hydrogenation yields no residual fuel oil, but rather motor fuel, LPG, and substantial quantities of valuable chemicals such as benzene, toluene, xylene, phenol, and others. Considering the type of products, steel requirements for coal hydrogenation are reasonable.

Commercial Coal-Hydrogenation Plants Needed

Some of the basic considerations of security that apply to oil shale are also applicable to coal hydrogenation. There is little question but that some time in the future domestic crude oil will have to be supplemented with liquid fuels from both coal and oil shale. The job will not be done with either alone.

United States coal resources are plentiful and widely distributed over many sections of the country. Coal-hydrogenation plants could be located in several large consuming areas. Taking advantage of the flexibility of coal hydrogenation by producing maximum quantities of chemicals would improve the economics of the process greatly. The immediate establishment of one or two coal-hydrogenation plants by private industry, as advocated by the Department of the Interior, could make a major contribution of needed chemicals and would help lay the groundwork for large-scale production of liquid fuels from coal should this become necessary for national security. It appears, however, that something in the way of Government incentives to private industry may be required at this time. Ebasco in its findings made the following statement: "We do not believe it would be feasible to finance the projects discussed in the Bureau of Mines report dated October 25, 1951, with private capital under conditions prevailing at January 1, 1951."

A summary follows of 1951 operations at each of the synthetic liquid fuels laboratories and demonstration plants of the Bureau of Mines:

Summary of 1951 Operations

Oil from Coal

Demonstration Plants, Louisiana, Mo.

During the past year, construction was completed and operations were started in the second of two Coal-to-Oil Demonstration Plants on the banks of the Mississippi near Louisiana, Mo. Prototypes of a new industry, both plants convert coal or lignite to high-quality synthetic liquid fuels and chemicals. However, they employ fundamentally different processing methods - coal hydrogenation and gas synthesis - in serving as proving grounds for American coals, equipment, and process modifications.

The Coal-Hydrogenation Demonstration Plant, a two-stage unit that operates at high temperatures and pressures, completed its second full year of experimental production. Two extended liquid-phase operations and one vapor-phase operation were carried out last year, and a third liquid-phase run was started for a total operating time of 150 "stream" days to December 1.

First, approximately 2,500 tons of western Kentucky coal was converted in two steps to nearly 350,000 gallons of gasoline, which was shipped to the military services for testing. Next, 2,500 tons of Illinois No. 6 coal was processed into vapor-phase charging stock. Then, liquid-phase processing of 4,400 tons of western Wyoming subbituminous coal was begun late in October. The products of these latter two liquid-phase operations will be converted to gasoline during the next vapor-phase run.

Each run was successful and achieved its objectives. Products were evaluated in Bureau and commercial laboratories and also passed road tests without difficulty, both in Bureau-operated vehicles and military fleet operations. The good quality of the gasoline, together with the quantity of aromatics and tar acids in the products, was significant.

Two integrated runs were made in the Gas-Synthesis Demonstration Plant. The first, started on September 4 and terminated on September 12 after achieving all objectives, was an orientation run to determine the plant's operability, complete the training of operators, observe the functioning of equipment and instrumentation, and reach as high a conversion rate as possible. The second, started on October 23 and completed November 18, showed that the Bureau's process is feasible, the equipment workable, the catalyst apparently long-lived, and the conversions in accord with those anticipated on the basis of pilot-plant results at Bruceton, Pa. The gasoline and Diesel oil produced during the run now are being evaluated.

Coal-gasification studies were continued at Louisiana, Mo., on a demonstration scale, and test runs in the oxygen-blown coal gasifier developed by the Bureau at Morgantown, W. Va., produced promising results. The synthesis-gas purification unit also was tested and proved capable of continuously reducing the impurities in the feed gas to less than 2 percent carbon dioxide and well under 0.05 grain total sulfur for each 100 cubic feet of gas.

In another operation, 75,800 pounds of iron oxide synthesis catalyst was produced at a cost of 16 cents a pound, not including plant amortization. Tests in bench-scale, pilot-plant, and demonstration-plant operations have shown this material to be as satisfactory as any catalyst previously tested.

Three major engineering cost estimates were made during the year. The original coal-hydrogenation plant cost estimate, based on a daily capacity of 30,000 barrels, was revised to comply with higher 1951 costs and with the advances in technical knowledge achieved in 3 years of demonstration-plant work. Two other cost estimates were made for 15,000-barrel-per-day plants, one using a southern Colorado bituminous coal and the other a northern Wyoming subbituminous coal.

Market surveys were continued to establish price and capacity trends for aromatic hydrocarbons, tar acids, and tar bases.

Laboratories and Pilot Plants, Bruceton and Pittsburgh, Pa.

Research at the Bruceton, Pa., laboratories and pilot plants on the synthesis of liquid fuel from gasified coal (Fischer-Tropsch and related processes), on the production of liquid fuel by hydrogenation of coal (Bergius and related processes), and on the gasification of coal in a vortex reactor has led to developments of theoretical as well as practical importance.

Oil was synthesized from hydrogen and carbon monoxide in a barrel-per-day pilot plant, using an internally cooled moving-bed reactor and a fused-iron catalyst. Although this plant was 13 times as large as those previously employed, no unusual difficulties were experienced during its operation.

The same catalyst was used in a number of slurry tests in which gas is bubbled through a catalyst powder suspended in oil. A problem of the catalyst settling was solved by adding modified bentonite to the slurry, increasing its viscosity. Uninterrupted experiments lasting 2 and 3 months thus were made possible.

Experiments on the Fischer-Tropsch synthesis at 500 to 1,500 p.s.i.g. pressure, with a nitrided fused-iron catalyst, showed little change of product distribution as compared to 100 to 300 p.s.i.g. pressure. The rate of the reaction, however, was not as sensitive to pressure changes in the higher range as it had been in the lower range of pressures.

Addition of alkali to iron Fischer-Tropsch catalysts was found to decrease the rates of carbiding and rereduction and to increase the rate of carbon deposition after carbiding was essentially completed. A method of preparing fairly pure Hagg iron carbide has been developed.

A combination of various physical and chemical analytical techniques was used to determine the constituents of the Fischer-Tropsch synthesis products. A scheme of mathematical analysis was devised to correlate the product compositions obtained with various catalysts and over a wide range of operating conditions. This correlation also predicts the maximum amount of any fraction of the product - Diesel oil, for example - that can be obtained under the most favorable conditions.

A pilot plant has been built for a continuous process of hydrogenating coal in a fluidized bed. Several coals also were tested in small autoclaves to determine their suitability for hydrogenation in the demonstration plant at Louisiana, Mo. Some were acceptable as received, while others first had to be dried and cleaned.

A study of the operating variables of the coal-hydrogenation process has shown that nickel, as nickel chloride, is the most suitable of the catalysts tested. It may be used in low concentration and produces a large amount of oil. A method for quantitative evaluation of the quality of coal-hydrogenation catalysts was developed.

For better utilization of the less-desirable products of coal hydrogenation, studies also are under way to find the best conditions (1) for obtaining gasoline by hydrogenation of the middle oil and (2) for recovering oil from the heavy-oil purge stream by steam stripping or coking. Preliminary results are promising in both instances.

New analytical procedures were devised for determining the composition of the products from coal hydrogenation, particularly that of the gasoline, tar acids, and tar bases.

Many of the variables of coal gasification, using steam and oxygen in a vortex reactor, have been explored and correlated. Introduction of part of the oxygen with the coal resulted in increased production of gas under otherwise equal conditions. The gasification reaction was diffusion-controlled above about 2,200° F., and complete gasification of coal appears possible in an adiabatic reactor under such conditions. With an optimum ratio of 7 to 7.5 cubic feet of oxygen per pound of coal, it is estimated that 34.1 pounds of coal and 247 cubic feet of oxygen at standard temperature and pressure are needed to produce 1,000 cubic feet of synthesis gas, a carbon monoxide-hydrogen mixture.

Abstracts of articles and patents pertaining to synthetic liquid fuels were compiled and published until recently, when lack of funds compelled suspension of this activity. A book on the Fischer-Tropsch reaction was published, and a bibliography on this process is being completed. The first two parts of a similar bibliography on coal hydrogenation were issued and the last part is being readied for printing. Reviews on the status of various aspects of this program were contributed to several journals, and translations of foreign articles of unusual interest in this field were made available as Bureau of Mines publications.

Synthesis-Gas Laboratory, Morgantown, W. Va., and Field Tests, Gorgas, Ala.

Planning for commercial-scale plants requiring large quantities of synthesis gas, both in this country and abroad, has emphasized the importance of the new developments in coal gasification. At Morgantown, W. Va., intensive work has been conducted on experimental development of pulverized-coal gasification with oxygen and steam. A high-pressure powdered-coal gasification process now being developed promises substantial reductions in the cost of synthesis gas, a major item of expense in manufacturing synthetic liquid fuels, ammonia, alcohol, and other chemical intermediates.

Experimental powdered-coal gasification units at the Morgantown station include:

(1) A small-scale gasifier handling about 50 pounds of powdered coal an hour and consisting essentially of a vertical tube about 6 feet high and 6 inches in internal diameter. This gasifier has provided data on the conditions under which coals can be gasified efficiently and also has proved valuable for evaluating the suitability of various types of coal for gasification.

(2) A new atmospheric-pressure gasifier, handling about 500 pounds of coal an hour, was completed during the year. Its design was worked out in

cooperation with Babcock & Wilcox Co., which also fabricated the unit. The performance of this gasifier with various arrangements of burners is being studied.

(3) A pressure gasifier completed in 1951 promises substantial economies in synthesis-gas production through reducing gas-compression costs. Designed to gasify 500 pounds of coal an hour at an operating pressure ranging up to 30 atmospheres or approximately 450 p.s.i., this unit in preliminary runs at 7 atmospheres showed high capacity, but rather severe erosion of the refractory lining occurred.

(4) Initial test runs in a pulsating flow or vibratory gasifier achieved extremely high throughput rates on the order of 1,000 pounds of coal an hour for each cubic foot of gasifier volume. However, erosion of the refractory lining again was experienced.

Gas-purification work at Morgantown included bench-scale experiments at elevated pressures to study the performance of (1) a copper-chromium-vanadium catalyst for simultaneous removal of hydrogen sulfide and organic sulfur from synthesis gas and (2) a copper catalyst for removal of small amounts of oxygen from synthesis gas.

As the recovery of sulfur must be a feature of the gas-purification system in any large Fischer-Tropsch plant, purification pilot-plant runs were made at 300 p.s.i.g. to study the selective removal of hydrogen sulfide from gases containing relatively large quantities of carbon dioxide. Among the purifying absorbents studied were triethanolamine, sodium and potassium carbonate, and tri-potassium phosphate. Carbon dioxide is believed to have a deleterious effect on the Fischer-Tropsch synthesis, and part of the purification program dealt with the removal of this compound from synthesis gas by using diethanolamine. Throughout most of the operations in the purification pilot plant, the total sulfur content of raw synthesis gas was reduced to less than 0.05 of a grain per 100 cubic feet.

At Gorgas, Ala., the second underground gasification experiment was completed. Continuous operation had been maintained for 22 months, and the coal underlying 2 acres of land adjacent to the original 1,450-foot entry was consumed. Drilling new inlets or outlets tangent to the perimeter of the burned-out area made it possible to extend the gasification over areas of coal land and also to improve the quality of the products. The experiment showed the importance of attaining good contact between the air or oxygen and the reacting coal faces. At the conclusion of the second experiment, the underground system was flooded with water and the fire extinguished.

A third experiment was started at Gorgas in which all underground mining was eliminated by using an electrolinking process tried earlier by the Sinclair Coal Co. and the Missouri School of Mines. Electrodes were inserted in the coal bed through boreholes drilled both for their installation and for subsequent use as air or gas inlets and outlets. A potential was applied to a pair of electrodes, causing a current to flow. The electric current heated and carbonized the coal, and the formation of coke increased the permeability of the coal bed. When the resistance of the system was reduced sufficiently, the electric current was shut off and air was pumped underground to carry on

gasification. An initial electrical linkage was formed between boreholes 67 feet apart and subsequently between boreholes 200 feet apart.

Gasification of a 67-foot section opened by electrolinking has been continued for 4 months with the production of combustible gases. As the throughput has been small, additional electrolinking will be attempted in the immediate future to increase the throughput and develop the system further.

Oil from Oil Shale

Experimental Mine, Rifle, Colo.

As problems associated with mining oil shale at low cost are nearer solution than other phases of the program, the scope of work was reduced considerably in 1951 at the Experimental Oil-Shale Mine on Naval Shale Reserve No. 1 near Rifle, western Colorado. Research activities were curtailed, and operations were directed primarily toward supplying the processing plant with oil shale.

Collection of drill cuttings from oil wells penetrating the Green River oil shale formations in the Rocky Mountain area was continued, but no additional data on potential reserves are available yet. As reported in 1950, an area of 1,000 square miles in Colorado could yield 300 billion barrels of shale oil from an oil-shale measure averaging 15 gallons per ton. Within this measure is the richer 30-gallon-per-ton Mahogany ledge that could yield nearly 100 billion barrels of shale oil.

The two sets of workings at the Experimental Oil-Shale Mine are known as the Selective Mine and the Underground Quarry. Initial production was from the Selective Mine, but the Underground Quarry has been supplying shale for the processing plant since 1949. Approximately 50,000 tons was mined from the Underground Quarry in 1951, and some 19,000 tons of this was transported to the processing plant.

In the mining and research program emphasis has been shifted to fundamental research. To this end, data were collected on the action of explosives by means of instrumentated tests and motion-picture studies.

The drilling phase of the mining-research program involves two separate investigations, percussion and rotary drilling. Several facts were recorded on percussion-drilling fundamentals, and the study of heat-treating procedures for minimizing drill-rod failures was continued, with notable success.

Rotary-drilling research showed that the bench level of a commercial oil-shale mine could be drilled by rotary methods at a considerable saving over percussion methods. Estimates are that bit and drill rod costs for rotary methods would be about \$0.01 per foot, compared to about \$0.028 per foot by percussion methods. In addition to the direct saving in bits and drill rods, the higher drilling rates achieved by rotary methods would lead to savings in such items as labor and power.

An exhaustive and continuous study of roofstone behavior has been conducted in an experimental test room in the Selective Mine since early 1947, when specialized equipment and apparatus were installed. By November 1948 the test room was 80 feet wide by 100 feet long. An extension to this room was completed in June 1951, making the total length 200 feet. Two rock falls occurred in the original section of the enlarged test room in August 1951, each consisting of a uniform slab 18 to 22 inches thick. Stratascope examinations of the roofstone in the Underground Quarry showed that no partings had developed at the 18- to 22-inch level.

In November 1950, a cost estimate was prepared for mining, crushing, and conveying 19,200 tons of oil shale daily to a processing plant. During 1951, revisions of this proposal were made to raise cost items to the January 1, 1951, price level. The revised estimated total cost of mining, crushing, and conveying oil shale to the retort stockpile is 47.63 cents per ton. This estimate includes management, depreciation, and taxes, but does not include depletion, profit, nor expenditures for off-site facilities.

Demonstration Plant, Rifle, Colo.

Pilot-plant activities in 1951 were concentrated on the gas-combustion process, a development of the Bureau's Oil-Shale Demonstration Plant near Rifle, Colo. In this continuous method of retorting oil shale, combustion of low-B.t.u. gas generated in the retort provides most of the necessary heat. All heating and cooling take place between gas and shale within the retort. Thus, neither exterior heat-exchange equipment nor cooling water, a scarce commodity in the West, is required. Furthermore, good yields are obtained at high retorting rates.

To evaluate the performance of the 6-ton-a-day gas-combustion pilot retort, a 4-day run was made on shale averaging 30 gallons a ton by Fischer assay, or about the grade that would be charged in a commercial operation. During the evaluation run, a yield of 95.7 percent by volume of Fischer assay was achieved at a retorting rate of 229 pounds an hour per square foot of cross-sectional area in the retort.

Related pilot studies included developing means of controlling oil-mist formation in the product cooling zone of the retort, investigating gas-air mixers, and testing equipment for separating the oil-mist from the gas stream.

Plans for a demonstration-scale gas-combustion retorting plant with a nominal capacity of about 300 tons a day were undertaken as soon as pilot-plant investigations had demonstrated that the process was sound technically. Through competitive bidding, the Blaw-Knox Construction Co., Chemical Plants Division, was awarded a contract for the design, fabrication, and erection of the demonstration unit, and it is anticipated that the new plant will be ready for operation in the summer of 1952.

Demonstration refining operations in 1951 provided much of the information needed for successfully adapting conventional thermal refining techniques to the processing of shale oil. Earlier runs in the experimental refinery had demonstrated the suitability of three thermal processes - visbreaking, recycle cracking, and coking - for making a virtually full range of liquid fuels from

the crude material. Logically, the next step was to ascertain, for those processes, the exact procedures and operating conditions that would give the best product quality and yields. Test operations also were conducted on thermal reforming, a process not investigated previously.

In an operation simulating the production of liquid fuels from oil shale on an industrial scale, a crude oil suitable for pipeline transportation was produced by visbreaking. Recycle cracking is an attractive method of refining the visbroken crude, because this process gives high yields of gasoline and permits the use of available thermal equipment at existing refineries. In a recycle cracking run on crude shale oil, a naphtha yield of 49.6 volume percent of the charge was attained, together with 45.9 volume percent residuum.

Experimental treating operations were continued in an effort to determine procedures and operating conditions by which the minimum amount of reagents consistent with desired results would be consumed. Recent addition of tetraethyllead blending facilities to the plant made possible the production of shale-oil gasoline that is being used in automobiles and buses at the station. Shale Diesel fuel has been in use on the project for almost 2 years. The performance of both appears to be equal to that of the corresponding petroleum products.

Through cooperative agreements, interested organizations contributed valuable additions to oil-shale technology. Sixteen new agreements were negotiated during the year, and four existing agreements were extended.

Under one new agreement, the Geneva Steel Co. tested a high-melting-point shale-oil pitch to determine its suitability as a blending component for preparing metallurgical coke from Utah coal. Under another, shale Diesel fuel was tested in a locomotive of the Denver & Rio Grande Western Railroad over a period of 751 hours. In both instances, results were encouraging.

Detailed cost estimates were made during the year for a nominal 250,000-barrel-per-day industry-scale oil-shale operation utilizing the newest developments in mining, retorting, and refining. The estimates include transportation costs to the west coast and are based on the Bureau's oil-shale-mining demonstration work and the gas-combustion retort developed by the Bureau. Two refining plans were considered, one incorporating basic thermal cracking and the other using a mild hydrogenation process developed by Union Oil Co. of California. Both refining options yield specification products; and, as would be expected, the hydrogenation process produces high yields of premium gasoline and Diesel oil.

Based on a capitalization of 50 percent equity and 50 percent borrowed funds, and with all products selling at current prices, the rate of return on the equity capital is estimated to be 8.4 percent after income taxes for the plan incorporating thermal refining and 11.2 percent when using mild hydrogenation to refine the crude oil. Although the thermal refining option is less economical, it has the advantage of utilizing refining processes that are in use at the present time and therefore would permit processing viscosity-broken crude shale oil in existing refineries.

Steel requirements for the industry-scale operation, including mining, retorting, refining, and a pipeline to the west coast, are 579,000 tons, or

about 3.0 tons per daily barrel of liquid fuel for the thermal cracking option and 555,000 tons, or about 2.8 tons per daily barrel of liquid fuel for the mild hydrogenation option. The thermal-cracking plan requires a larger pipeline, hence the higher steel requirement.

Laboratories and Pilot Plants, Laramie, Wyo.

For two major reasons, the attention of the staff at the Bureau's Oil-Shale Experiment Station in Laramie, Wyo., was centered during the past year on development of a process for retorting oil shale at high temperatures: (1) Critical chemical products now in short supply can be produced in this manner, and (2) the type of retort that appears most suitable for this high-temperature operation also shows promise of extremely high throughputs in the normal retorting temperature range.

Before tentative design for a small pilot plant was developed, three methods of retorting at high temperatures were studied: (1) The inclined-surface retort, somewhat similar to a conventional coal-carbonization retort except that the retort tube was set at an angle to permit continuous flow of shale; (2) a single-vessel fluidized-bed retort; and (3) an entrained-solids retort in which the shale is carried into and out of a heated, vertical furnace by an entraining gas or steam. Of the three methods, the entrained-solids retort appears to offer the best possibility of enlargement to pilot-plant and commercial-plant size, and a small pilot plant employing this principle is now being constructed.

In refining research, efforts were directed toward developing methods for treating thermally cracked shale gasoline and improving distillate stocks for use either as Diesel fuels or catalytic cracking stocks. As background for the gasoline treating research, extensive studies were made of the properties of this type of gasoline and the polymer formed when it is acid treated. This work has resulted in a catalytic treating method that appears to have advantages over those previously used. It indicates also that low-temperature acid treating itself may be essentially a catalytic-treating process and suggests lines of investigation that may result in improved acid-treating techniques.

Solvents have been found that are more effective in preparing catalytic-cracking stocks and Diesel fuels from shale-oil distillates than those studied in the past. Equipment has been constructed for use in extending the study of hydrogenation of shale oil and shale-oil distillates to pressures above 1,500 p.s.i., the maximum safe operating pressure for equipment previously available. Now virtually ready for operation, this new equipment will permit more-complete evaluation of the hydrogenation process as a method for refining shale oil.

Compositions and properties were determined for two series of oil shales from the Experimental Mine that assayed from 10.5 to 75 gallons of oil a ton and were representative of minable beds in the Mahogany ledge. The data, published in a Bureau of Mines report of investigations, included the results of petrographic and X-ray examinations, determinations of shale properties, ultimate and oxide analyses, assays and examinations of assay products, and weathering tests.

The constitution of organic material in Colorado oil shale was studied by degrading it into smaller organic fragments for analysis and identification. The degradation methods included oxidation by alkaline potassium permanganate and nitric acid, hydrolysis with hydrochloric acid and potassium hydroxide, extraction with organic solvents, and destructive distillation, or heating. The results indicated that the organic material consisted preponderately of nonbenzenoid structures. Aromatic and terpene structures appeared to be present in minor amounts, but they were either of low molecular weight or were readily susceptible to oxidation.

Knowledge of the composition of shale oil still is sketchy, but it is vastly greater than that available a few years ago. It has been augmented during the past year by publications on pyrroles identified in shale-oil naphtha, gum formation in shale-oil naphtha, and determination of nitrogen in shale oil. Presentations before technical societies included papers on mass spectral correlations in composition studies, composition of crude shale oils, and oils from high-temperature retorting.

Recent analytical research has emphasized composition studies on three types of shale-oil products, the oils from high-temperature retorting, and the primary naphtha and heavy gas-oil fractions from N-T-U crude oil. In addition, work has been done on the development of analytical methods.

Tar acids recovered in refining thermally cracked gasoline from N-T-U crude shale oil were purified by removing the nitrogen- and sulfur-containing constituents, tar bases, carboxylic acids, water, and polymers to produce phenol, cresols, and xylenols of commercial quality.

Tar bases, also a byproduct of shale-oil gasoline refining, were treated to remove impurities and stabilized to reduce gum and color formation. Tests showed that the purified bases, when added to refined shale-oil gasoline, had no detrimental effect on its stability, and an increase in the octane rating of the gasoline was realized.

PART I

PROCESSING, COAL-TO-OIL DEMONSTRATION PLANTS, LOUISIANA, MO.

Coal-Hydrogenation Demonstration Plant

Two extended liquid-phase runs and one vapor-phase run were completed in 1951. A third liquid-phase operation is under way. On December 1 the combined operating time was 150 stream-days. Approximately 2,500 tons of Western Kentucky coal was converted into nearly 350,000 gallons of 77.5 motor method or 83.5 research octane gasoline, which was shipped out for military testing. An additional 2,500 tons of Illinois No. 6 coal (see fig. 2) was converted into vapor-phase charging stock, and the liquid-phase processing of 4,400 tons of subbituminous coal from Lake DeSmet, Wyo., was started in late October. Products from the latter two liquid-phase operations will next be converted to gasoline in a single vapor-phase run.

It should be noted that, throughout this section of the report, the data presented refer to coal actually processed. Coal was required for the production of steam, power, and filtered water but is not included. Furthermore, the hydrogen was made from natural gas.

Pertinent operating information is included, and processing data characterizing and finally comparing the hydrogenation of Rock Springs, Wyo., Western Kentucky, and Illinois No. 6 coals are summarized in tables 1 through 5, with appropriate discussions. A complete report is in preparation for each coal run and will be published in the form of a report of investigations. Significant and steady progress in the development of techniques, equipment, and technical data is producing the results required for the economic commercial production of fuels and chemicals from coal by the hydrogenation process, and these results are outlined in the following progress report.

Earlier operations included a short vapor-phase run made on North Dakota lignite-tar distillate oil in 1949, followed in 1950 by four comparatively short exploratory liquid-phase runs and one vapor-phase run, all on Rock Springs coal. These operations helped to train operators and work out the many changes required for improved plant performance.

TABLE 1. - Analyses of coals (moisture-free basis)

<u>Proximate</u>	<u>Wyoming</u> <u>(Rock Springs)</u>	<u>Western Kentucky</u> <u>No. 11 bed</u>	<u>Illinois</u> <u>No. 6</u>
Volatile matter	45.1	39.4	42.9
Fixed carbon	49.5	53.4	48.8
Ash	<u>5.4</u>	<u>7.2</u>	<u>8.3</u>
Total	100.0	100.0	100.0
<u>Ultimate</u>			
Hydrogen	5.3	5.2	5.0
Carbon	72.3	74.2	72.3
Nitrogen	1.5	1.4	1.4
Oxygen	14.4	9.2	9.9
Sulfur	1.1	2.8	3.1
Ash	<u>5.4</u>	<u>7.2</u>	<u>8.3</u>
Total	100.0	100.0	100.0
Heating value	12,970 B.t.u.	13,390 B.t.u.	13,020 B.t.u.
<u>Over-all material balance - Illinois No. 6 coal</u>			
Input:			
M.F. coal (includes catalyst)	114,250 lb.		
Pasting oil	168,210		
Make-up hydrogen gas	<u>23,425</u>		
Total input		305,885 lb.	100 percent
Recovery:			
Light oils	59,490		
Heavy oil (includes H.O.L.D.)	192,040		
Off gases	<u>26,620</u>		
Subtotal	278,150 lb.		
Water and soluble salts	<u>15,765</u> lb.		
Total recovery		293,915 lb.	96.1 percent
Unaccounted for		11,970 lb.	3.9 percent
Hydro yields (recovery)			
Hydrocarbon gases	3.84 M c.f./ton, m.a.f. coal		
Light oils	3.52 bbl./ton, m.a.f. coal		
Heavy oils39 bbl./ton, m.a.f. coal		

TABLE 2. - Typical operating conditions and yields in liquid-phase hydrogenation

	Wyoming (Rock Springs)		Western Kentucky No. 11 bed		Illinois No. 6
	Period 1	Period 2	Period 2	Period 5	
Pressure p.s.i.g.	10,200	8,100	8,300	8,400	7,900
Temp. 1st converter °F.	870	866	865	864	866
2d converter do.	874	892	866	865	861
Paste injection g.p.t. ^{1/}	550	520	456	465	486
Coal, m.f. t.p.d.	54.7	53.4	54.9	65.4	57.1
H ₂ gas to stalls M cu. ft./ton	194.5	182.0	171.5	138.0	188.1
Purge gas do.	28.2	30.7	10.9	5.9	5.6
Products from hydro:					
H.O.L.D. g.p.t.	223.6	214.3	175.5	166	214.5
C.C.P. product net g.p.t.	341.9	336.8	279.0	276	265.0
Gasoline g.p.t.	37.2	43.7	37.9	36.8	19.3
Naphtha do.	-	-	27.8	39.5	44.7
Middle oil do.	125.0	117.8	68.9	43.4	70.6
Flushing oil do.	12.4	-	-	-	4.0
L.O. bottoms do.	167.3	175.3	144.3	156.1	126.5
Total vapor-phase charging stock recovered					
..... bbl./ton m.a.f. coal	4.07	4.06	3.44	3.07	3.52
Net heavy oil produced bbl./ton	-0.20	-0.10	0.69	0.79	0.39
Total oil produced bbl./ton m.a.f. coal	3.87	3.96	4.13	3.86	3.91
Liquefaction percent of m.a.f. coal	96.4	96.0	96.2	96.7	94.2
Gasification (C ₄ and lighter) M c.f./ton	7.18	6.98	4.01	3.98	3.5
Weight percent on m.a.f. coal do.	26.7	26.4	13.7	13.2	12.1
Hydrogen consumption:					
Total percent m.a.f. coal do.	15.1	14.5	10.8	10.0	9.7
Reaction percent m.a.f. coal do.	9.1	8.3	6.5	7.25	6.8

^{1/}G.p.t. - gallon per ton of moisture-free coal.

TABLE 3. - Typical analytical data from liquid-phase hydrogenation

	PASTING OIL			COAL PASTE			H.O.I.D.			C.C.P. PRODUCT			GASOLINE			NAPHTHA			MIDDLE OIL			LIGHT-OIL BOTTOMS		
	Wyoming (Rock Springs)	Western Kentucky No. 11 bed	Illinois No. 6	Wyoming (Rock Springs)	Western Kentucky No. 11 bed	Illinois No. 6	Wyoming (Rock Springs)	Western Kentucky No. 11 bed	Illinois No. 6	Wyoming (Rock Springs)	Western Kentucky No. 11 bed	Illinois No. 6	Wyoming (Rock Springs)	Western Kentucky No. 11 bed	Illinois No. 6	Wyoming (Rock Springs)	Western Kentucky No. 11 bed	Illinois No. 6	Wyoming (Rock Springs)	Western Kentucky No. 11 bed	Illinois No. 6	Wyoming (Rock Springs)	Western Kentucky No. 11 bed	Illinois No. 6
Distillation.....°F.																								
I.b.p.	475	475	477				591	360	485	190	190	184	96	79	83	306	210	219	412	242	390	547	592	590
5 percent	573	560	566				628	550	580	396	240	224	115	95	105	340	312	276	454	434	455	607	622	631
10 percent	595	604	596				646	606	609	434	297	288	134	118	118	354	360	349	484	464	483	625	638	639
20 percent	627	636	627				660	646	647	535	390	383	183	141	139	362	378	377	512	494	505	646	654	656
50 percent	706		674						702	618	593	576	262	214	186	382	402	404	550	534	535	695	686	696
70 percent			698							674	668	655	334	294	214	394	418	420	572	552	555	730	712	730
90 percent											731	740	400	399	315	420	446	455	603	578	586	795		
E.P.		680					686	680	734	712	750		420	418	370	460	516	501	638	610	625		760	756
Recovery, percent.	49.0	70.0					80.0	81.0	60.0	84.0	93.5	90.0	92.6	89.9	93.3	99.0	99.0	98.3	98.1	99.0	98.2	90.0	87.0	74.0
Sp. gr. or °A.P.I....	1.18	1.117	1.107	1.30	1.20	1.222	1.33	1.25	1.238	10.2	11.2	11.5	50.7	58.5	63.3	18.9	17.1	17.9	11.8	12.0	11.8	1.07	1.06	1.06
C ₆ H ₆ - P.E. insol...	25.3	8.4	7.03	55.6	41.3	46.5	46.5	25.2	24.4															
C ₆ H ₆ insol.	16.7	5.5	5.38	49.9	43.7	44.6	34.5	19.0	20.1															
Tar acids										13.3		20.7	5.7	2.1	0.6	24.0	38.0	35.3	15.8	22.0	23.6			
Tar bases										0.6		0.2	3.6	1.7	1.4	2.2	0.9	0.5	2.0	0.1	0.0			
Aromatics													15.9	19.2		32.8	36.5		45.4	54.7				

TABLE 4. - Typical operating conditions and yields in vapor-phase unit

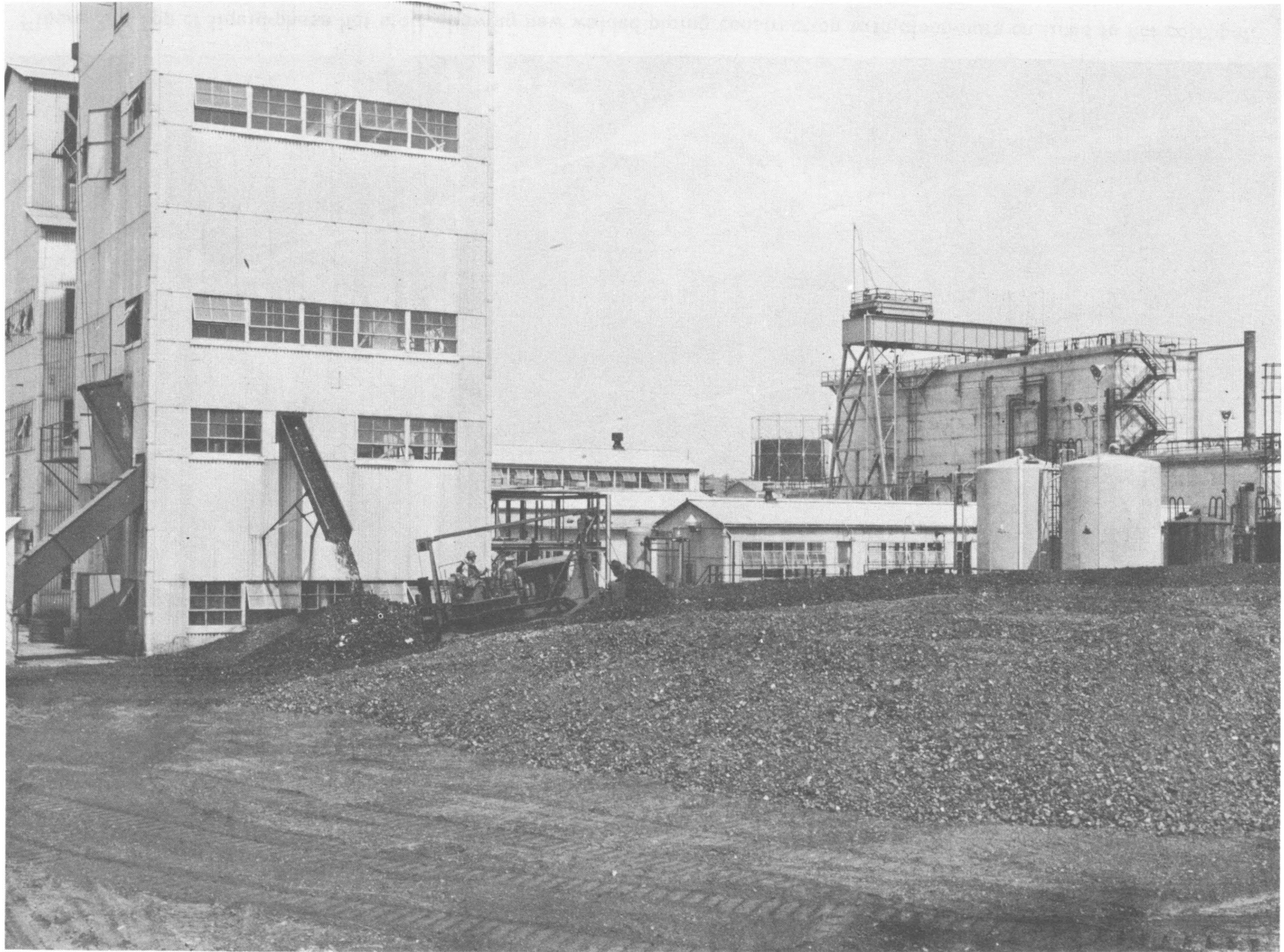
	Wyoming (Rock Springs)	Western Kentucky No. 11 bed	
		Period 1	Period 2
Pressure p.s.i.g.	10,200	10,250	10,250
Converter temperatures:			
Average middle of catalyst beds ... °F.	876	887	898
Average bottom of catalyst beds ... do.	890	905	916
Catalyst	Zn-Cr-Mo	Zn-Cr-Mo	Zn-Cr-Mo
Feed:			
Injection gal./day	16,680	20,320	22,180
Virgin do.	11,860	10,370	14,550
Recycle do.	4,820	9,950	7,630
Gas flows:			
Make-up hydrogen gas M c.f./day	1,008	1,037	1,114
Total gas to stall do.	9,200	8,670	9,360
Purge gas do.	745	58	29
Products from hydrogenation:			
Catchpot liquid, net gal./day	17,110	21,530	22,710
Gasoline do.	11,930	11,380	15,080
Wash oil do.	360	-	-
Bottoms do.	4,820	10,150	7,630
Stabilized gasoline..bbl./bbl.virgin feed	1.01	1.09	1.04
Gasification (C ₄ and lighter)			
M c.f./day	145.	90.	118.
Weight percent on feed consumed	14.3	9.6	8.9
Space time rate			
Feed lb./cu. ft. catalyst/hr.	51.37	65.4	69.5
Gasoline produced do.	29.07	29.9	39.8
Reaction hydrogen			
..... weight percent on virgin feed	3.5	5.4	4.2

TABLE 5. - Typical analytical data from vapor-phase hydrogenation

	FEED			PRODUCTS														
	To hydrogenation			Cold catchpot			Raw gasoline			Wash-oil naphtha			Bottoms			S. S. gasoline		
	Wyoming coal (Rock Springs)	Western Kentucky		Wyoming coal (Rock Springs)	Western Kentucky		Wyoming coal (Rock Springs)	Western Kentucky		Wyoming coal (Rock Springs)	Western Kentucky		Wyoming coal (Rock Springs)	Western Kentucky		Wyoming coal (Rock Springs)	Western Kentucky	
		No. 11 bed			No. 11 bed			No. 11 bed			No. 11 bed			No. 11 bed			No. 11 bed	
		Period	Period		Period	Period		Period	Period		Period	Period		Period	Period			
1		2	1		2	1		2	1		2	1		2	1		2	1
Distillation ...°F. I.b.p.	144	196	149	131	147	135	94	87	88	184	Non Produced	Non Produced	400	369	368	75	87	79
5 percent	214	324	203	180	186	172	116	114	108	280			410	390	386	111	136	95
10 percent	262	376	270	199	216	195	140	134	133	311			422	401	399	157	211	133
20 percent	338	404	365	228	262	231	170	164	164	336			426	411	407	249	310	179
50 percent	436	458	443	317	377	342	228	228	222	371			444	439	432	360	378	382
90 percent	548	577	570	472	505	488	336	331	327	397			514	543	524		444	440
E.P.	614	625	615	562	588	568	376	364	366	425			604	610	591	464	462	472
Recovery, percent	96.7	97.8	96.9	98.2	98.0	98.5	98.0	94.4	97.0	99.1			99.0	99.0	99.3	80.5	92.5	93.0
Gravity, °A.P.I..	28.3	21.0	25.2	41.9	39.3	42.4	54.5	55.2	55.6	33.1			25.7	24.8	24.4	51.3	51.9	53.4
Tar acids	9.4	9.8	12.1	1.2	0.8	1.4	0.4	0.7	0.7	-			2.4	1.5	1.8	-	-	-
Tar bases	3.2	0.8	1.2				0.6	0.4	1.0		0.8	0.1	0.1					
Aromatics	46.8	52.2	45.6				25.2	27.1	25.6		61.4	58.5	60.6					

AVERAGE TESTS ON FINISHED GASOLINE PREPARED FOR FLEET ROAD TESTS

	Wyoming	Western Kentucky			Wyoming	Western Kentucky	
		Period 1	Period 2			Period 1	Period 2
Octane rating (A.S.T.M. D908-48 T.C.F.R. Research Method)	83	-	-	Distillation, °F.			
Octane rating (A.S.T.M. 357-48 C.F.R. Motor Method)	78	76.6	76.7	I.b.p.	92	97	98
Vapor pressure Reid p.s.i.g.	9.0	10.0	9.0	10 percent	136	130	124
Gravity °A.P.I. at 60° F.	54.8	53.3	54.8	50 percent	225	225	212
Sulfur content percent	.3	-	-	90 percent	318	328	328
Doctor test (FST 520.31)	Neg.	Neg.	Neg.	95 percent	336	354	351
Corrosion test (A.S.T.M. D-130-30)	Neg.	Neg.	Neg.	E.P.	366	381	372
Existent gum mg./100 ml.	1.0	1.2	4.0	Recovery, percent	99.0	97.6	98.0
Induction period min.	720	-	-	Residue, percent	1.0	1.2	1.0
Tar acids	Nil	0.7	0.9				



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Figure 2 - 2,500-ton pile of Illinois coal ready for processing.

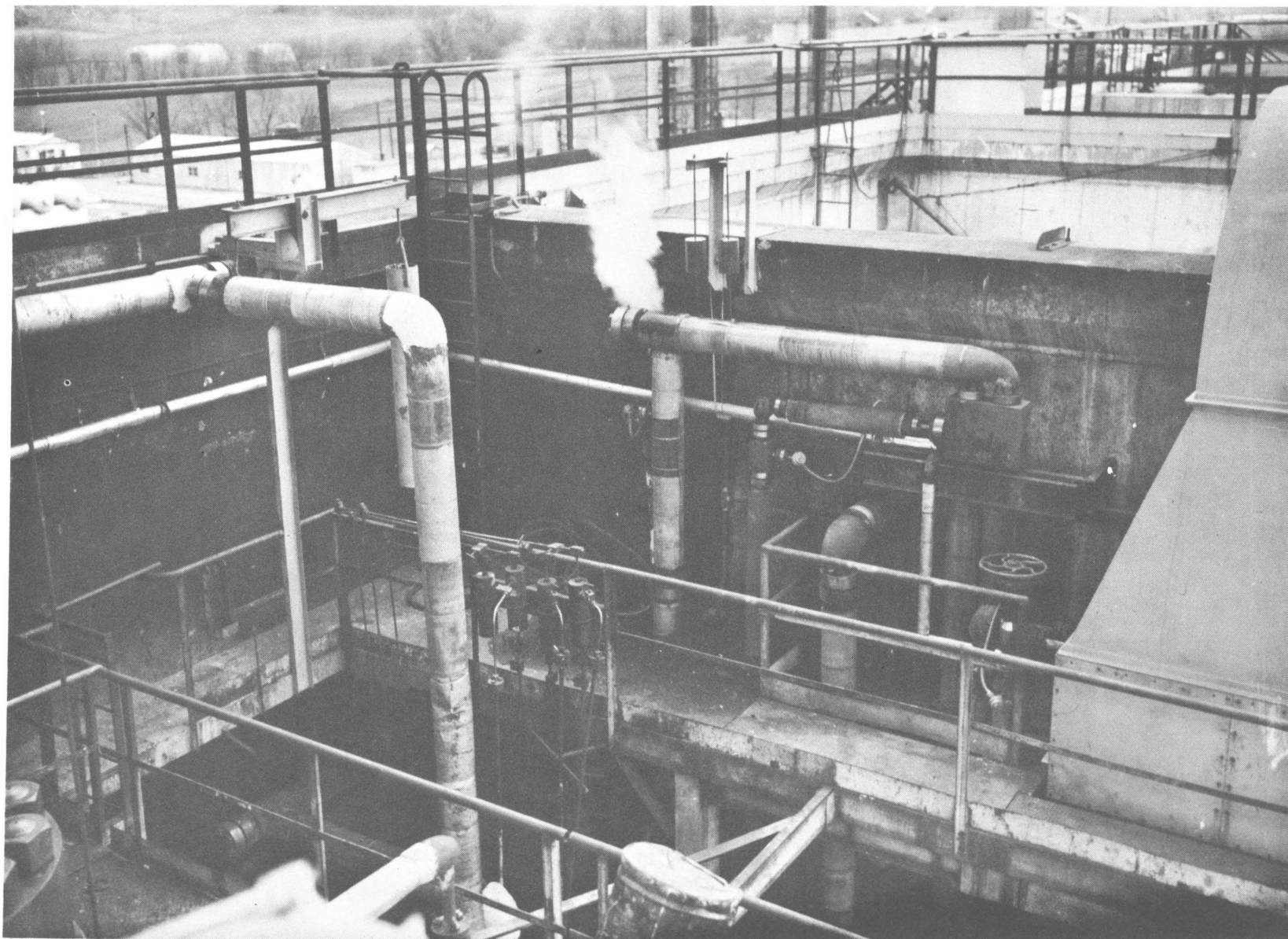


Figure 3. - Top of liquid-phase hot stall, showing new welded piping construction with clean-outs on lines to hot catchpot.

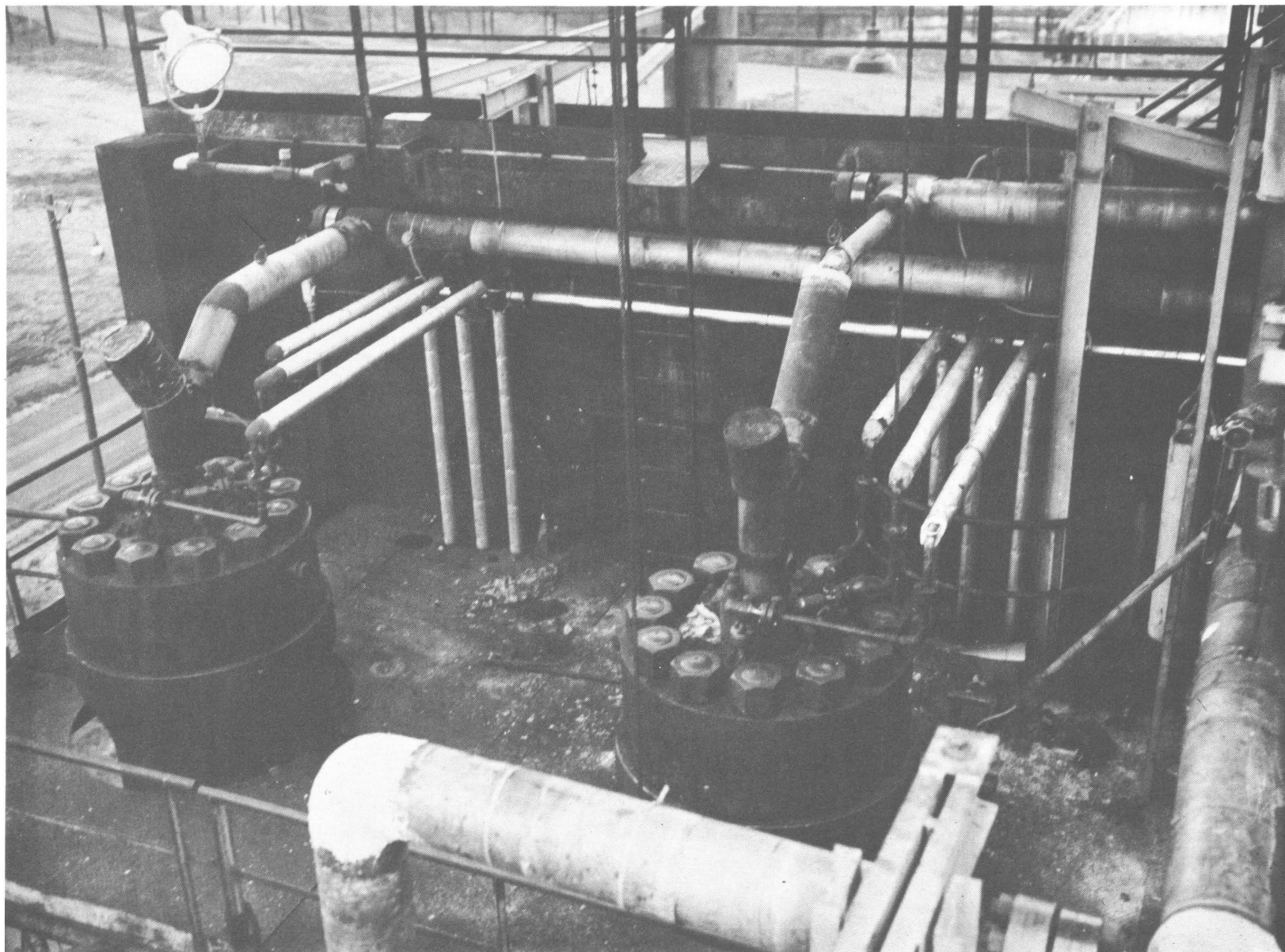


Figure 4. - Top of liquid-phase hot stall during turn-around, showing **new welded lines** from converters and flexible supports.

Operations

The exploratory runs on Rock Springs coal supplied valuable products and the information required to solve many difficulties which had interfered with safe, continuous operation. After major changes in equipment and techniques, it was possible to process 2,500 tons of coal in a single continuous liquid-phase run. Experience and observations determined that:

1. The chevron-type packing was satisfactory for use in high-pressure injection pumps, provided it is properly supported and is lubricated enough at the low-pressure end. Months of test experience with a dozen or more packing arrangements, using both metallic and nonmetallic materials, resulted in replacing expensive machined-metal packing with low-cost, easily replaceable, neoprene-impregnated duck. The packing was developed in cooperation with a leading manufacturer, who now supplies similar material to several commercial users.

2. All flanged joints in the hot piping systems, if not required for assembly and clean-out, must be eliminated, and the long piping runs must be properly anchored and flexibly supported to avoid high stresses and resultant leaks in the remaining joints. The original hot piping installation, using flanges and flanged fittings indiscriminately, was patterned generally after German practice, and within a few months contributed directly to three emergency shut-downs and one fire. Substitution of welded connections, wherever possible, made it relatively easy to secure and maintain a tight system (see figs. 3 and 4).

3. The improved, 3-percent-chrome-steel, injection pump blocks with exterior ball valves performed satisfactorily at moderate speeds. Although the workability of this unconventional design, adopted as a stopgap measure, was unknown, pumps did not vapor-lock or become clogged with solids.

4. The wash-oil hydrogen-purification system required revisions to prevent hold-up and carry-over in the high-pressure scrubbing tower, troubles that had interfered with compressor and instrument performance and prevented the efficient removal of hydrocarbons and nitrogen in maintaining hydrogen purity with minimum fresh hydrogen usage. Spasmodic operation of the scrubber over a period of several months proved that the equipment needed modification to provide better cooling of the incoming gas, better distribution of the scrubbing oil, adequate liquid-disengagement space above and below the packing, and maintenance of a constant liquid level by an instrument arranged with both the top and bottom take-off points from the free space below the packing.

5. It was found that the flash-distillation solids-removal unit must be separated from the high-pressure unit because the direct withdrawal of hot heavy-oil let-down (H.O.L.D.) seriously interfered with hot catchpot level control and did not provide a uniform flow at a satisfactory temperature for flash distillation. Provisions were made to allow feeding from a tank through a separate heater under close automatic control. The residue-removal system requires further improvement, because the original pumping installation is inoperable, and a stopgap method using an open trough is inefficient and somewhat hazardous.

6. Difficulties with instrument control, particularly of levels, were attributable to variations in system pressure. These variations occurred in attempting to maintain pressure by varying the make-up hydrogen input while maintaining a uniform rate of purge. It was proved that fixing the rate of hydrogen input and varying the purge for pressure control maintained uniform system pressure and gas quality required for smooth operation.

7. The continuous horizontal Bird centrifuge removed benzene-insoluble material from the H.O.L.D., but equipment of this type is not satisfactory for adjusting the asphalt level of the pasting oil.

8. The liquid-phase converter volume had to be reduced to achieve satisfactory control of reactions and to lessen the tendency for solids to deposit in the converters. The converters originally were lined to leave 130 cubic feet free space in each. However, the plant was not generally sized for converters of such generous proportions, and early results proved they must be reduced in volume to 90 cubic feet each by use of smaller-diameter liners.

9. Extensive use must be made of properly sized, strategically located, restricting orifices and target assemblies downstream of control valves, particularly when solids were handled, in order to achieve satisfactory valve life. This is true especially of let-down valves when operating at system pressures above 8,000 p.s.i.

10. It proved necessary to discontinue using rotary pumps in paste-circulating service because these pumps would not maintain enough head pressure and capacity for acceptable periods. Neither the original valveless screw pumps nor the replacement gear pumps proved satisfactory, and it was necessary to replace them with steam-driven duplex pumps equipped with hardened rods, Madsen valves, and Darcova cup plungers. The application of specially equipped reciprocating pumps to this difficult pumping duty is a marked advance over previously known methods of handling extremely viscous high-solid-content liquids.

Liquid-Phase Run 6 (Western Kentucky Coal)

During an extended winter shut-down, the liquid-phase system was completely cleaned and inspected, and mechanical work required in adopting the above changes was completed. After the usual pressure testing and activation of instruments and controls, coal was charged to the unit from March 30 to May 17. During the run, 2,160 tons of moisture- and ash-free (m.a.f.) coal was processed, and the inventory of light oils was increased by 291,500 gallons and the heavy oils by 43,500 gallons. This dried, washed coal, containing 7.2 percent ash, hydrogenated well to light oil (vapor-phase feed) at a conversion pressure of 7,700 p.s.i. and temperature of 875° F., using a 0.5-percent iron catalyst. Coal was hydrogenated at rates of 50 to 75 tons per day, with excellent conversion and control results.

All equipment in the stall and high-pressure area remained tight throughout the entire run. Despite high paste rates and considerable injection-pump valve trouble, which developed as the run progressed, flow, pressure, and temperature conditions remained relatively smooth and controllable throughout the run. The rather frequent difficulties with ball valves in the paste pumps were

traced to partly plugged suction lines. Accordingly, these lines were re-designed to alleviate plugging and to facilitate cleaning before inadequate suction conditions developed (see fig. 5). It is hoped that spring loading of suction valves also will improve packing and plunger life, as well as the over-all injection-pump performance (fig. 6). While the service life of most high-pressure control valves was excellent, the performance of heavy-oil let-down valves continued somewhat erratic (3 to 7 days) despite the installation of 3/32-inch restricting orifices immediately downstream from these valves. Hot-catchpot level-control difficulties were accentuated by a tendency for reaction to start in the vessel, causing deposits of coke. To alleviate these conditions, more agitation gas is now being used and arrangements have been made for adding hydrogen or flushing oil as quench to the inlet-product tube. The wash-oil scrubber with the revised level-control arrangements worked very well. During the run, arrangements were completed for a desander line to facilitate removal of fine, sandy solids from the converters during operation and to assist in emptying these vessels on shut-downs.

The flash-distillation system was operated about half of the time, usually along with the Bird centrifuge, partly to reduce further the solids in the pasting oil but primarily to control the asphalt level of the oil. The fume problem and the manpower requirements of the process remained serious obstacles to continuous use of the unit. An experimental run, dropping part of the residue on a small, water-cooled metal conveyor, gave promising results. Arrangements for obtaining and installing this type of solids-removal equipment are under way.

Five periods were selected during the run for yield and process analyses. Period 1 lasted from April 7 to 14 and represented a low-throughput run with 0.1 percent stannous oxalate catalyst. Period 2 was from April 18 to 25 and represented a low throughput on mixed catalyst (0.05 percent stannous oxalate and 0.8 percent copperas). Period 3 covered April 29 to May 4 and represented gradually increasing throughput with 2.5-percent copperas catalyst addition and lower reaction temperatures. Periods 4 and 5 were from May 4 to 8, and from May 8 to 13, respectively, with a high throughput and 2.4-percent copperas catalyst addition. A division into periods 4 and 5 was made because preliminary calculations indicated an increased liquefaction beginning May 8.

Data from periods 2 and 5 are presented in summary form, in figure 7 and tables 1, 2, and 3. From the tabulated data it is possible to draw some comparison between the hydrogenating properties of the coals and the effect of mechanical and process improvements. It should be noted that this was the first run during which the solids-removal system functioned adequately at all times to maintain an average pasting oil of 5.5 percent benzene insolubles and 8.4 percent petroleum-ether insolubles, as opposed to the previous 16.7 percent benzene insolubles and 25.3 percent petroleum-ether insolubles. This improved pasting oil allowed the average percentage of coal in the paste to be raised from 35 to 43; converter-coal throughput increased from 18 to 30 pounds per cubic foot of reactor volume per hour. The higher-unit coal throughput and the improved converter temperature, flow, and pressure conditions resulted in a lowered asphalt production and a decrease in apparent gasification from 26.5 to 13.5 percent. As a result of this and the lower oxygen content of the coal (that is, 9.2 percent as opposed to 14.4 percent in Rock Springs coal), the reaction hydrogen was only 7.0 percent for Western

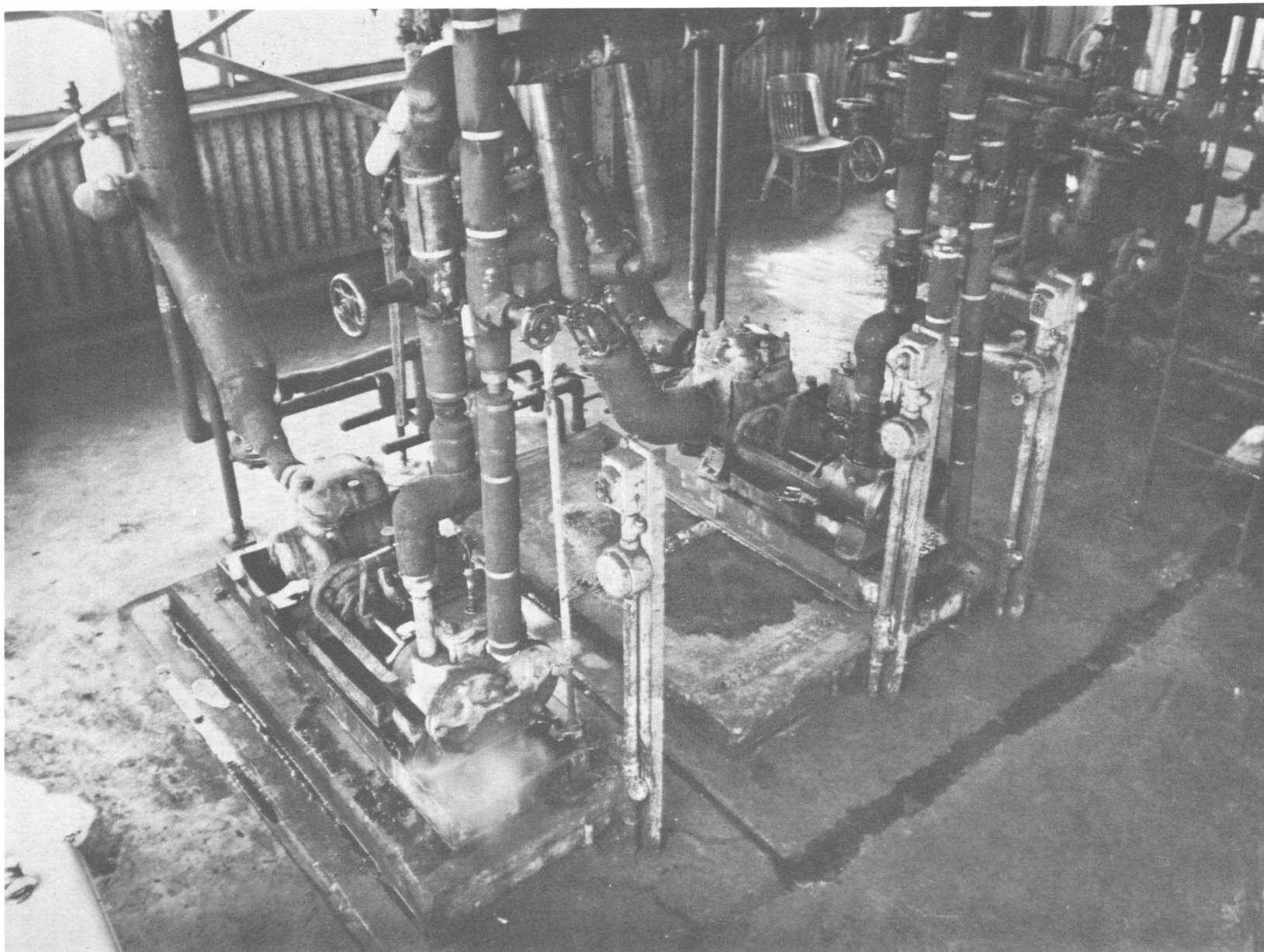


Figure 5. - New piping arrangement in paste-transfer pumps P-6A and B.

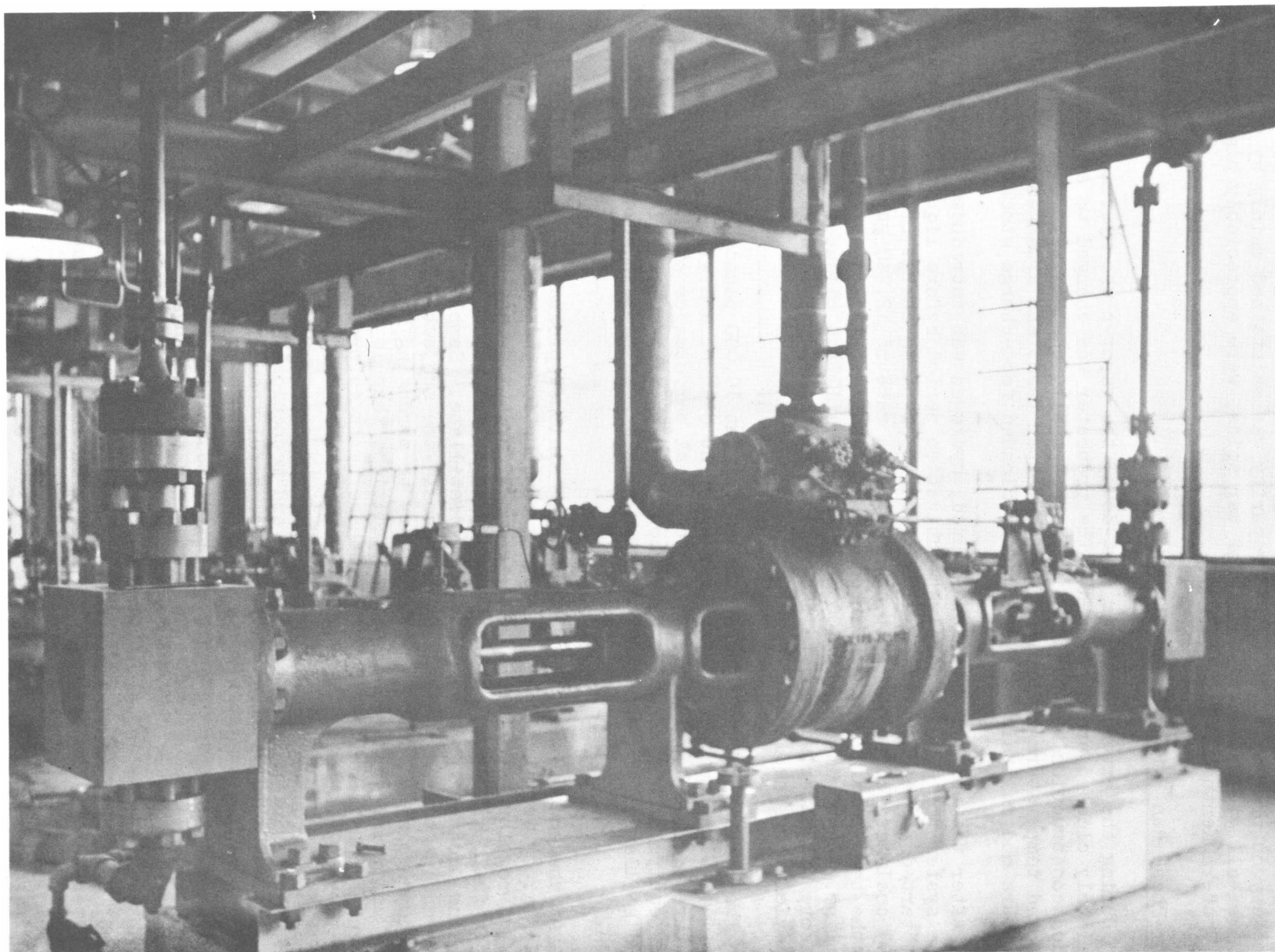


Figure 6. - High-pressure injection pump.

Kentucky coal compared to 8.7 percent for the Rock Springs coal. The greatly improved operation of the hydrogen wash-oil system resulted in a loss of hydrogen to purge of only 5.9 M cubic feet per ton of coal against 30.7, which was necessary on previous runs when the purity was maintained mainly by purge. The over-all yields, particularly of tar acids, were appreciably higher for the Western Kentucky coal.

Vapor-Phase Run 3 (Western Kentucky Coal)

During the extended winter shut-down, the vapor-phase system also was completely cleaned and inspected. The preheater was changed to series flow, welded construction was adopted in the hot stall, changes were made to obtain improved temperature control of the converter feed, and arrangements were made to secure and maintain more accurately blended feed-charge stock.

After the unit was pressure-tested, hydrogen was introduced to the vapor-phase system for a 3-day catalyst-activation period before liquid-phase feed was started for a 30-day run. The fresh vapor-phase charge from Western Kentucky coal was fed to the unit at an average rate of 12,740 gallons per day, and the total charge was converted to an average of 12,713 gallons per day of gasoline. Approximately 60,000 gallons of distillate produced from slop and creosote oil later was fed to the unit at a slightly reduced rate for comparable yields of gasoline.

The operations were performed smoothly at 10,000 pounds per square inch (p.s.i.), with the inlet to the converter at 845° F. and with average bed temperature of 900° F. The over-all mechanical performance of the high-pressure plant equipment was adequate throughout the run. Likewise, all equipment in the distillation and gas-manufacturing plants remained satisfactory at all times.

At the end of the run the following finished products from the refinery (see fig. 8) were available for plant consumption and testing: 225,000 gallons of regular gasoline, 7,000 gallons of aviation-base stock, 400 gallons of jet fuel, all from Western Kentucky coal, and 60,000 gallons of regular gasoline produced from creosote-slop distillate. Samples of the first three items and gasoline from Rock Springs coal were subjected to complete tests in a commercial laboratory, preliminary to arranging for military performance tests under more severe operating conditions than is normally required of post transport equipment. A summary of these tests is presented in a later section of this report.

A number of interesting process and mechanical improvements contributed materially in making this run more successful than previous operations. The smooth, dependable operation of injection pumps and recycle compressors allowed smooth flows to the unit at all times. Inasmuch as the preheater was repiped to operate all tubes in series and the exchanger was provided with better insulation, it was possible to hold the outlet temperature from the heater within a relatively narrow operating range. The new, close-range (800° to 900° F.) recording-temperature controller regulating cooling gas to the preheater outlet line kept the converter-entrance temperature within the $\pm 2^{\circ}$ F. required for smooth control of bed temperatures.

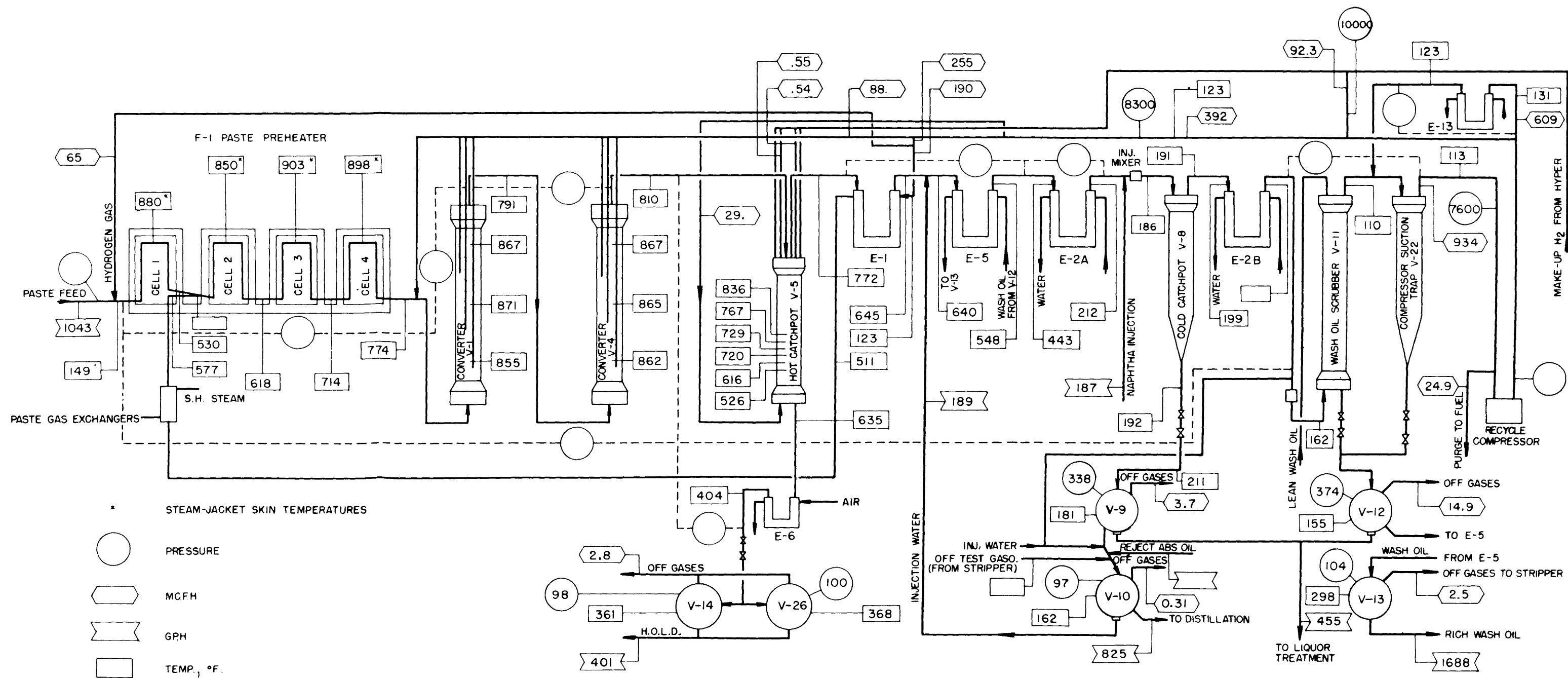


Figure 7. - Liquid-phase hydrogenation unit; typical operating conditions for period 2, Western Kentucky coal hydrogenation.

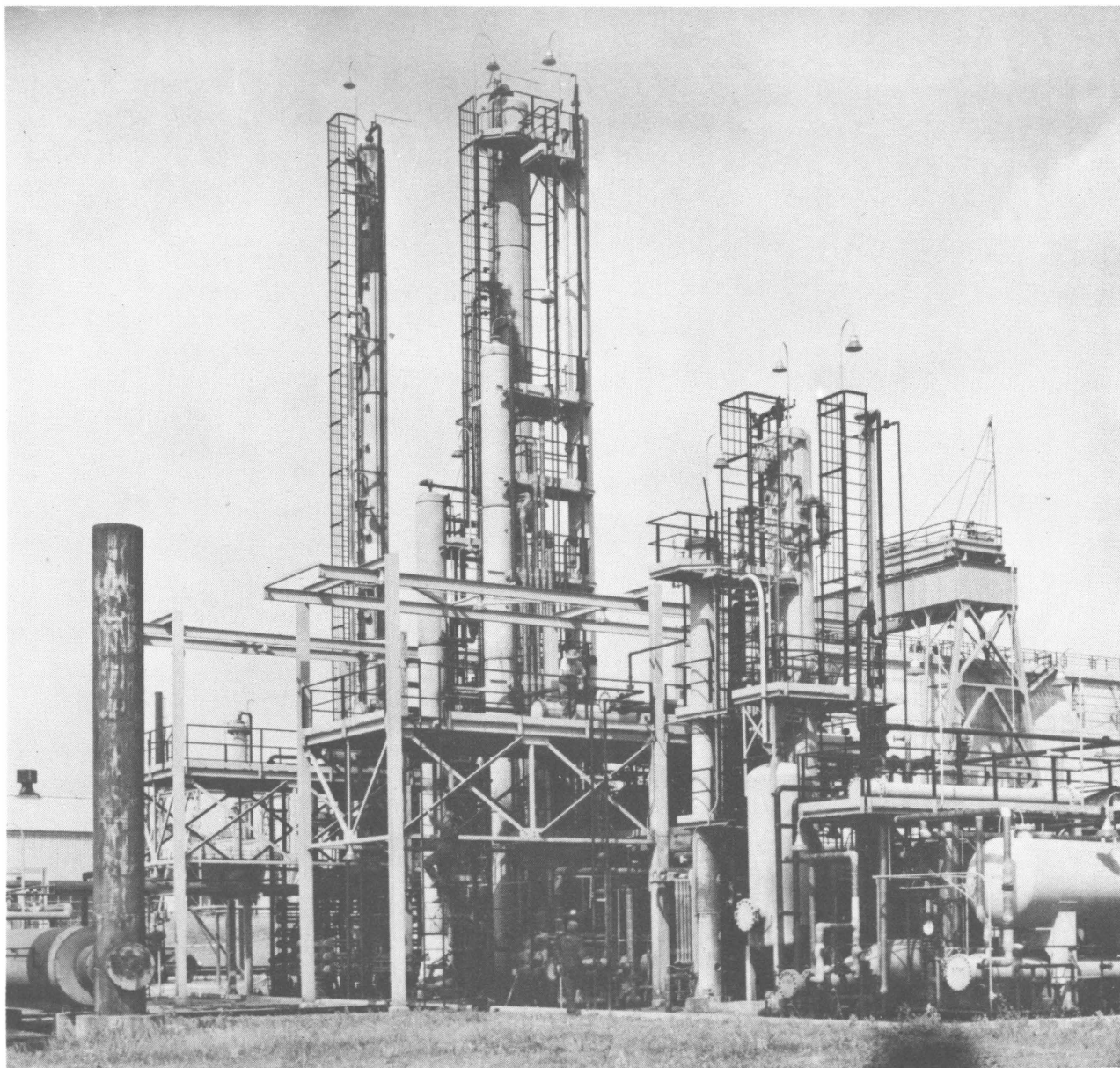


Figure 8. - Refinery undergoing exchanger and insulation repairs.

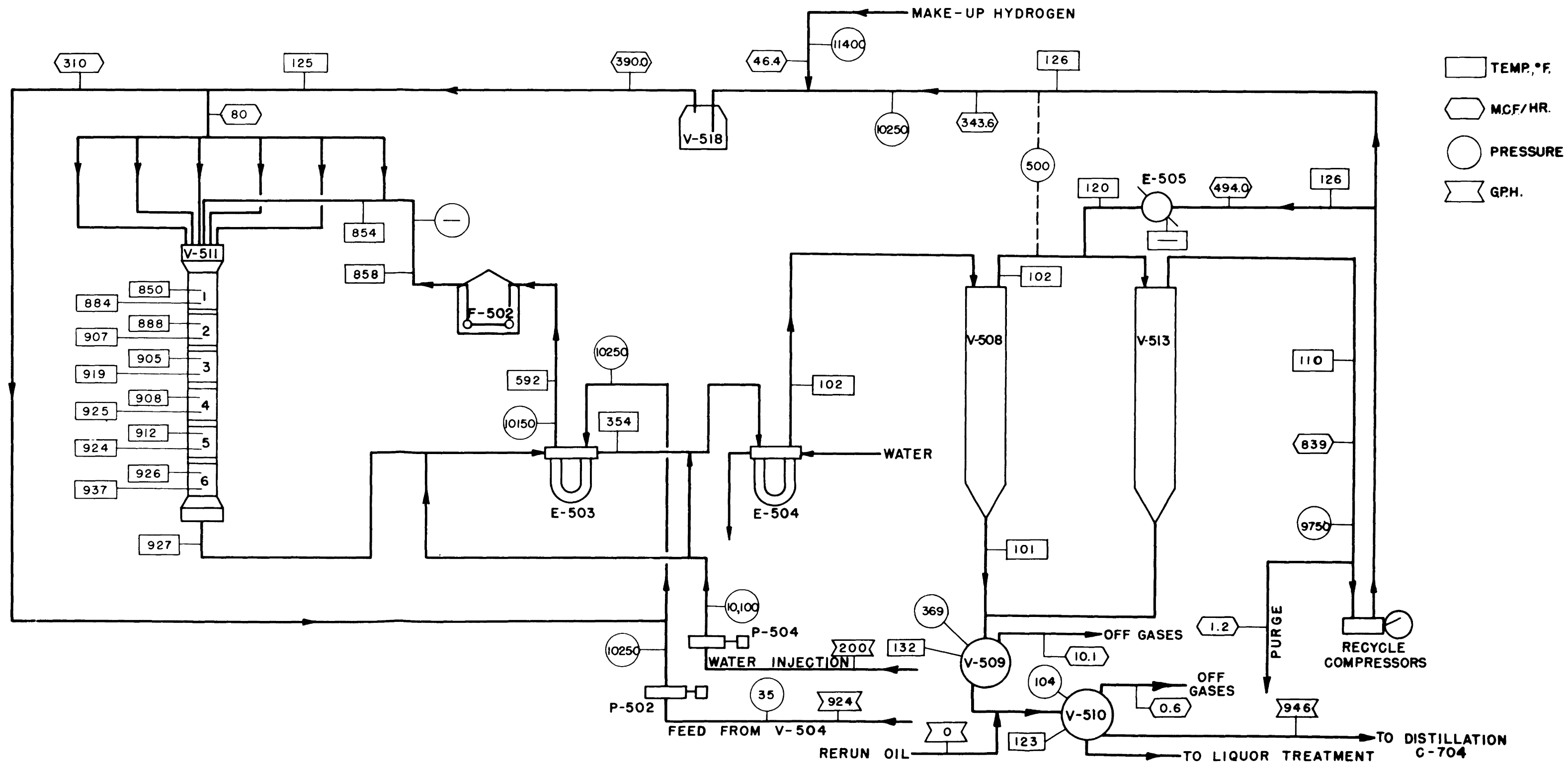


Figure 9. - Vapor-phase hydrogenation unit; typical operating conditions for period 2, Western Kentucky coal hydrogenation.

No serious difficulties were experienced with inaccurate pyrometer temperature readings and very few control-valve tips became worn or broken during the run to interfere with smooth let-down or other flow conditions. As many of the flanged joints were replaced by welds and the piping was properly supported and anchored, there was no leakage, even during periods when the operating temperatures changed rather abruptly. All of the cooling gas lines were recently steam-traced, and no difficulties were encountered in maintaining a free flow of cooling gas to the catalyst-bed levels.

Improved operations in the distillation area resulted in a more perfectly blended feed stock.

Despite improved converter inlet-temperature conditions, the feed-product heat exchanger is being changed to minimize uneven flow of liquid and gas, subsequent overloading of the fired heater, and uneven temperatures to the converter.

Data from these operations are presented in summary form in figure 9 and in tables 4 and 5. It will be noted that the Western Kentucky vapor-phase charge was lower in American Petroleum Institute (A.P.I.) gravity and higher in tar-acid content than the Rock Springs charging stock. However, due largely to improved converter control, it was possible to process the Western Kentucky material at a 20 percent higher rate and yet produce gasoline equivalent to the Rock Springs gasoline as regards octane and aromatics content. The gasification was somewhat higher for the Rock Springs feed, and the hydrogen usage was higher for the lower-gravity, higher-tar-acid content Western Kentucky stock. The lower gasification of the Western Kentucky stock, 9 percent versus 14 percent for Rock Springs, was reflected in a 5 percent higher gasoline yield.

Liquid-Phase Run 7 (Illinois No. 6 Coal)

During the vapor-phase run, the liquid-phase system was prepared for run 7. In addition to more or less routine cleaning, inspection, and maintenance, a new top pyrometer tube was installed in the hot catchpot, and provisions were made for tripling the hot catchpot agitation gas.

After pressure testing and activation of instruments, 15 percent coal paste was charged to the unit on August 12, 1951. The coal concentration was gradually increased until, within 2 days, the fresh-coal content of the paste was 40 percent. The run progressed smoothly at a rate of about 52 tons per day of moisture-free coal, until 6:45 p.m. on August 15, when all pyrometer indications in the second converter suddenly read off scale. Although there was no appreciable change in hydrogen purity or consumption, hot or cold catchpot products, or in other temperatures in the system, to be on the safe side it was assumed that there was a hot spot in the second converter. The feed was changed to 50-50 paste and pasting oil, and the converter was cooled with a full flow of cooling gas for several hours. When all converter temperature indications again became normal, full paste operation was resumed at moderate temperatures.

After closely observing the unit on August 16, it was concluded that any hot spot in the second converter had been of minor nature. Further investigation proved that the thermocouple wiring was charred and shorted above the

36-foot level. A new thermocouple assembly was installed the next morning, and normal operation at 870° to 880° F. was resumed on August 17.

During the following days, the coal rate was gradually raised to 65 tons per day under conditions simulating the 30,000-barrel-per-day commercial-plant estimate. Operations were smooth until 6 p.m. August 19, when a second minor hot spot developed in the second converter, and a third occurred the following evening. These disturbances apparently did not seriously interfere with satisfactory throughput for the 65 ton-per-day operation from August 18 to 21. On the morning of August 22, while attempting to raise the second converter temperature from 860° to 870° F. to decrease the hot catchpot product and increase the vapor-phase feed make, temperatures up to 1,200° F. were attained quite suddenly elsewhere. In view of the doubtful condition of temperature-measuring equipment, cooling gas tubes, and solids-formation conditions in the second converter, on August 22 it was decided to circulate the unit down for inspection, cleaning, and repairs to the converter as required.

Upon inspection it was found that the second converter contained a solids formation extending from a point 10 feet above the bottom to within a few feet of the top. The first converter and the hot catchpot were checked by a displacement method and found to be free of solids formation.

The following measures were taken to correct the hot-spot conditions:

- (1) A new control valve was installed to provide automatic control of the bottom temperatures of the second converter.
- (2) All cooling gas lines were steam-traced and insulated to prevent plugging.
- (3) The catalyst addition, calculated as Fe, was to be increased from 0.5 to 1.0 percent.
- (4) Paste-gas flows were to be increased by 10 percent.
- (5) Second converter temperatures would be held a few degrees higher than the first converter temperatures.
- (6) A new arrangement was made to install the pyrometer-tube thermocouple wiring to give less chance for thermocouple failures.

Paste injection for run 7B was begun September 2. Operation proceeded smoothly as temperatures, flows, and paste concentrations were raised to obtain a rate of 65 tons of moisture-free coal per day. On September 9 the unit was switched to pasting oil for 5 hours, owing to stoppage of the coal flow by a piece of metal jamming the Star feeder on the Waytrol unit.

High throughput production was started when enough data were obtained for the operation as outlined. The coal throughput was gradually raised to reach a 77- to 80-ton-per-day rate. To obtain the desired light-oil yield, the converter temperatures were slowly increased to a maximum of 885° F. After these conditions were attained and held for 5 days, trouble developed September 20 because of a local hot spot in the bottom of the second converter. Temperatures recorded by the two lower temperature controllers quickly went off scale,

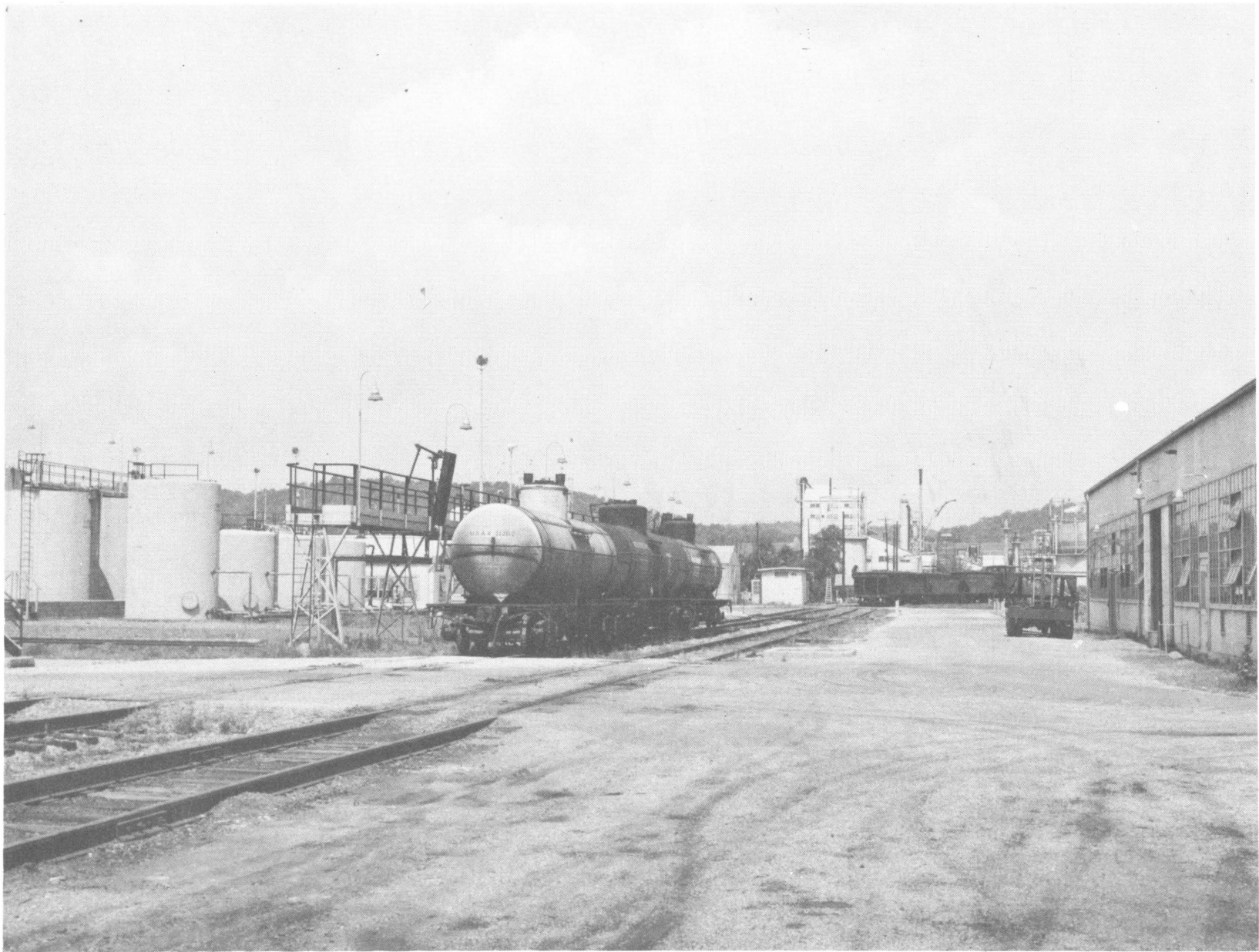


Figure 10. - Illinois No. 6 coal entering plant and gasoline awaiting shipment to Army.

but a controller for the upper section of the converter recorded a top of only 950° F. The outlet temperatures dropped below normal as soon as cooling was begun. Conditions did not indicate a runaway reaction, but rather a local hot spot that could spread to a serious runaway if not quickly controlled. The unit was switched to pasting oil, and the converter temperatures were reduced to less than 800° F. The second converter top and midpoint temperatures dropped rapidly, but the bottom temperature was much slower to respond, indicating some deposition of solids.

It is of interest that some European experience indicates that the throughput can be increased above a given rate, but the maximum temperature that can be held in the converters reaches an upper limit, dependent upon the stall pressure. Above this temperature, local hot spots and a tendency toward ragged operation, with possibilities for runaway reactions, will develop. The converter temperatures were below the maximum point indicated by experience on German coals.

After the converter temperatures dropped below 800° F., injection of coal paste was resumed, using a 50-50 mixture of pasting oil and paste. The unit was returned to normal operation with 46-47 percent coal paste, and it was decided not to continue the high throughput operation, as some deposition of solids was suspected in the second converter. Therefore, the unit was operated at a 60- to 65-ton-per-day rate for several days, until it was deemed advisable to adjust conditions to obtain data for producing a 50-50 yield of heavy oil to light oil. On October 1, with the supply of coal exhausted, the unit was circulated down for a normal shut-down. Cleaning of the last row of preheater tubes and removal of some relatively soft solids from the second converter, together with inspection and mechanical work, were accomplished by October 29, before starting run 8 to process 4,400 tons of subbituminous coal from Lake DeSmet, Wyo.

Data from the processing of Illinois No. 6 coal (see fig. 10) are presented in summary form in tables 1, 2, and 3.

The comments after liquid-phase run 6, comparing the results from processing Rock Springs, Wyo., and Western Kentucky coals, apply in general equally well to the processing of Illinois No. 6 coal. Due in part to the relatively low oxygen-content of Illinois No. 6 coal, the gasification and process hydrogen usage were about 10 percent lower than for Western Kentucky coal. The oil and tar-acid yields were essentially the same and equally good for Illinois and Western Kentucky coals.

Mechanical Features and Plant Improvements

Preparation of Coal and Paste

By performing the coal-preparation unit operations on a 2-shift-per-day basis, it was possible to dry and pulverize 60 to 75 tons per day of moisture-free coal. During the later runs ferrous sulfate catalyst was used in place of tin oxalate. In autoclave bench-scale investigations, it had been found that excellent results could be obtained from this catalyst by spraying a water solution on the raw coal before drying and pulverizing. This method was tried but was discontinued, because the coal, already saturated with water, did not readily absorb the solution. The addition of wet catalyst was discontinued in favor of adding dry iron sulfate to the coal in the primary crusher, a method

that worked quite successfully and, for the coals processed to date, has given satisfactory hydrogenation results.

To lower the moisture content of the hot recirculating flue gas used to dry coal and to improve sizing of the ground coal, arrangements are under way to install a cooler in the recirculating flue gas line and to replace the ineffective pulverized-coal classifier with a vibrating screen.

The paste-making equipment operated more satisfactorily and dependably than in previous years. This was attributed to added provisions for external lubrication of bearings submerged in the paste mixer and to added adjustable support arrangements to prevent the lower blades from rubbing the tank bottom.

Although continuous operation is still difficult, the mechanical functioning of the coal Waytrol was improved. To obtain more accurate weighing, especially at high throughput rates, it is planned to increase the speed of the Star feeder and the Waytrol belt. Plans also are under consideration for batch-weighing the coal from the Redler conveyor into the powdered-coal bin.

Pumps

Two standard duplex reciprocating pumps, equipped with crown valves, special liners, and Darcova cup pistons, are now used for paste circulation with excellent results.

Considerable trouble is still experienced with the oversized centrifugal paste-oil-circulation pumps, which leak excessively around the packing. By installing new bearings and sleeves, and providing for adequate clearance between the housing and impeller to eliminate excessive pressure against the packing, the situation has been improved considerably and the packing life increased from, in some cases, a few hours operation to 15 days or more. A smaller, steam-driven, heavy duty centrifugal pump of open end impeller-type construction is on hand for trial runs before testing pumps, similar to those used for circulating paste.

Many improvements have been made in the design and operation of the high-pressure injection pumps. These included harder, more accurately machined plungers, spring-loaded packing, and improved lubrication to the outer end of the packing. The suction and discharge ball valves, located in flanged fittings midway of the plunger travel, continue to give 7 to 24 days service. In the case of paste pumps, valve life has been materially lengthened by improving the suction conditions, that is, constant paste-circulating pressure, and revised suction manifolds to facilitate periodic cleaning before serious plugging occurs. However, an entirely satisfactory valve has not been developed for paste service. The injection pumps in clean light-oil service have shown increased capacity and dependability after introduction of spring-loaded suction valves. As the service life of the new blocks also is limited, a new injection pump has been designed, using compound cylinder construction, centrally located steam drive, and lubricated spring-loaded flexible packing. The first simplex pump has been delivered, installed, and is in operation; the others are in production.

Instruments and Controls

Instrumentation of the plant is believed to be more complete than in any other domestic or foreign high-pressure plant. The instruments include liquid level, flow, pressure, and temperature controls, and most of these function dependably. Except in the converters, temperature measurement has been fairly satisfactory. The response of skin thermocouples used on lines carrying suspended solids is slow and the indicated temperatures are 20° to 70° below the actual temperatures, even when well-insulated and with no appreciable coke deposits on the pipe walls. Improved paste-preheater temperature control has been achieved by controlling from the skin temperature of the steam-jacket tubes rather than from the heavy-wall-product tubes.

Temperature measurements in pyrometer tubes have been made more accurate and reliable by carefully assembling the small, fiber-glass-covered thermocouple wires inside a small inner tube rather than around a tube or rod. The couples emerge through small slits into which the spring-clip contact points can recess, and the wiring and contact points are protected in this way. Reliability of the temperature measurement has been improved by careful cleaning, polishing, and drying of the heavy-walled pyrometer tube. Means are sought to measure converter temperatures, using short couples through the walls, particularly in the vapor phase, as the present outer catalyst support tube surrounding the heavy-walled pyrometer tube seriously interferes with thermocouple-temperature response. The measurement of paste and other solids-containing oils requires improvement. An area flowmeter and the displacement meters proved unsatisfactory, although venturi-type flowmeters appear to have some promise for this service. Meanwhile, the paste rate is approximated from tank gages, injection-pump strokes, and preheater-temperature indications. The measurement of small flows, particularly in the refinery, has been improved by use of 50- and 100-inch meters in place of 20-inch meters.

Although the initial operation was promising, the gagetron has not yet proved serviceable for control of hot catchpot level. However, entirely satisfactory service has been achieved from the pneumaticator system since using filtered fresh hydrogen and somewhat shorter bottom tubes, which are not adversely affected by the increased flow of bottom agitation gas required to keep the vessel clean. Temperature measurements of the liquid and vapor in the vessel and of the streams flowing from the vessel have proved very useful in checking the level and the quantity of flow from the vessel.

A major improvement in diaphragm-control-valve operation can be largely attributed to the modified, well-lubricated, soft-metal base packing and to use of better valves, plugs, and seats.

Stellite No. 1 plugs and seats are adequate in clean liquid or cooling gas services. In gas and solids bearing oil service, such as H.O.L.D., Kennametal (tungsten carbide) has given the best results. Norbide (boron carbide) was tried but has not given good performance, owing largely to imperfections in manufacturing the plugs and seats.

Further tests are in progress to develop restricting orifices and target devices that will allow the valves to function without excessive wear, mainly in starting and stopping the flow.

Heaters and Exchangers

The performance of the steam-jacketed paste preheaters and the direct-fired vapor-phase heater has been proved. Direct-fired paste-heater designs have been proposed for commercial plants and tests on unjacketed tubes will be tried, using the demonstration-plant heater and starting with a few hairpin tubes in the first heater section. The steam jacket already has been removed from the hydrogen heating-tube hairpin, with good results. The vapor-phase heater has been repiped for series flow, the temperature control has been improved, and tendencies toward hot tubes and subsequent coke formation have been alleviated.

Double-tube heat exchangers gave satisfactory service, except for the seven-parallel-pass, vapor-phase, feed-product exchanger, which has been removed for alterations. Several small shell and tube heat exchangers are on order, and tests will be scheduled to obtain data for commercial design.

High-Pressure Vessels, Piping, and Fittings

The original high-pressure piping materials have proved quite satisfactory. However, it seems that a considerable increase in allowable stresses may be permitted by the use of other materials that would decrease the cost of commercial plants. Cooperative work is under way to test the suitability of centrifugally cast steel tubing for high-pressure work.

The demonstration plant incorporates much more welded construction than did European hydrogenation plants. Our operating experience to date indicates this to be justified, and additional welding is being introduced into hot, high-pressure alloy lines. An extended period of operation will be required to confirm the practicability of this step. If and when confirmed, commercial plants may use welded construction with a minimum number of flanged joints for assembly, inspection, and clean-out purposes.

In adopting this construction, the hot stall piping was removed and re-fabricated to eliminate as many flanged joints as possible. For clean-out connections, a welding tee was used, with a blind lens ring and a blind flange to close the opening. A system of counterbalanced weights supported the hot piping. After the initial pressure test was made, hot stall piping was heated to an average temperature of 800° F. to permit observation of line growth and performance of the counterbalancing. Only minor corrections were necessary to allow for free expansion of the lines in the proper direction. With the new piping construction and through close attention in assembling flanged fittings and vessel heads, leakage problems in the stall area have become negligible.

Equipment for Removing Solids

Both the Bird centrifuge and flash-distillation unit have been used during the year for removing solids. Because the Bird centrifuge does not have the capacity to remove all the solids and has little effect on the asphalt level, it was necessary to operate flash distillation at maximum rates most of the time. By this means, it was possible for the first time to maintain the benzene-insoluble solids in the pasting oil between 4 to 7 percent and the asphalt,

particularly sticky asphalt, at a low level, where its presence seldom interfered with pump packing, strainers, or other equipment and instruments.

The speed of the Bird centrifuge was increased from 2,000 to 2,340 revolutions per minute (r.p.m.) in an attempt to improve separation of solids. At this higher speed, it was impossible to operate the centrifuge at a rate much over 800 gallons per minute (g.p.m.) without overloading and breaking shear pins. Many pins were sheared during runs; and at one time, when straight H.O.L.D. was being processed, it was necessary to remove the rotor and conveyor for cleaning, owing to the formation of a solid cake that cemented the rotor and conveyor together.

The flash-distillation unit was revised extensively, and it was operated early in the year to process the heavy, solid-bearing oils from liquid-phase run 5. H.O.L.D. is supplied from tankage and heated to 650° to 700° F. in a radiant-type furnace. A spray condenser system was installed to condense most of the exhaust steam from the quench tower and recover oil entrained in the steam. The most troublesome problem encountered was handling of pitch from the bottom of the flash drum. The original Magma plunger pumps proved inadequate, mainly because it was impossible to prevent plug-up from solids and keep the suction line, pumps, and discharge line hot enough to assure flow at all times. After many attempts, the pumps were abandoned in favor of a chute leading directly from the bottom of the flash drum into a portable receiving tank, which is hauled away and emptied. A test was made on a water-cooled conveyor to handle the pitch. The test looked promising, and a full-scale conveyor is on order.

Corrosion and Erosion Experience

Corrosion in low-pressure carbon-steel equipment is similar to that found in oil refineries. It is most severe on the water side of heat exchangers. In one exchanger installed in 1949 and operated less than 80 days, 18 tubes out of 84 corroded through from the water side. Heat exchangers and vessels handling gases and liquids containing hydrogen sulfide and other sulfur compounds have had relatively high corrosion rates. The liquid-phase overhead exchanger has corroded at the rate of 0.02 inch per year. Based on actual operating time, this rate would be 0.08 inch per year. The liquid-phase reflux drum corroded at the rate of 0.01 inch per year, or 0.04 inch per year based on actual operating time. Other exchangers and vessels have corroded at similar rates, and in some cases there has been extensive pitting. In the high-pressure equipment corrosion was not severe, although equipment using water, either as a coolant or as process liquid, was affected. The water-injection pumps and the suction manifolds have pitted, and some scale has formed. Tubes in box-type coolers have scaled on the outside and pitted near the water line. There has been no significant corrosion on the inside of tubing or equipment handling the hydrocarbon-process liquids.

Erosion has been more serious than corrosion. The heavy-oil-let-down, containing a high percentage of ash, unconverted solids, and absorbed gases, has caused deep erosion where velocities approach the speed of sound. Throttling-control valves made of the most abrasion-resistant metals, in some instances, have been eroded beyond use in less than 24 hours. The normal life of these

parts when less than 500 gallons per hour (g.p.h.) is handled has been under 48 hours. Modifications of design and changes in materials are being made to attempt to increase their life. Two 1-inch high-pressure elbows, which followed a restricting orifice in the lines handling this material, were cut completely in less than 3 weeks' operation. These 1-inch elbows were replaced with 2-1/2-inch high-pressure tees having solid-shaped plug target which deflected the material in the same manner as an elbow. Three weeks' operation of these units resulted in fairly severe erosion of the plugs and tees. The wear plate in the vessel was also deeply eroded. A replaceable plug having a spherical cup, hard-faced with abrasion-resistant metal, then was tried. This change virtually eliminated the wear on the tees and has reduced erosion of the wear plate in the vessel considerably.

Evaluation of Hydrogenation Fuel Products

Motor Gasoline

Extensive fleet tests in Army ordnance transport and engineer equipment have shown that the synthetic gasoline (see fig. 11) will give fully satisfactory performance under sustained 100-percent-overload conditions. Use of the gasoline in all Bureau of Mines equipment at the Louisiana, Mo., Station also has been successful. To evaluate the products further and extend the military test program, samples of finished vapor-phase gasoline made from Rock Springs and Western Kentucky No. 11-bed coals, an aviation base stock, and a blended jet fuel from Western Kentucky No. 11-bed coal were submitted to a commercial testing laboratory for evaluation. The tests are summarized in the following tables:

<u>Finished gasoline</u>	<u>Western Kentucky No. 11 bed</u>	<u>Rock Springs, Wyo.^{1/}</u>
Gravity, °A.P.I.	54.1	54.3
10 percent evaporation °F.	125	135
50 percent evaporation do.	220	224
90 percent evaporation do.	327	320
Residue percent	1.0	1.0
Vapor pressure p.s.i.	9.9	8.4
Octane number:		
Motor method	77.3	75.3
Research method	83.7	81.5
Existent gum content mg./100 ml.	1.6	4.0
Sulfur content percent	0.023	0.016
Corrosion copper strip	Negative	Positive
Oxygen stability minutes	480+	480+

Composition after removal of phenols and bases, percent

Aromatics	29.5	25.2
Olefins	2.5	1.8
Naphthenes	26.2	28.1
Paraffin content	41.8	44.9
<u>Aniline point</u> °C.	26.4	28.0

^{1/} The gasoline from Rock Springs coal had been stored in a 55-gallon drum for 1 year.

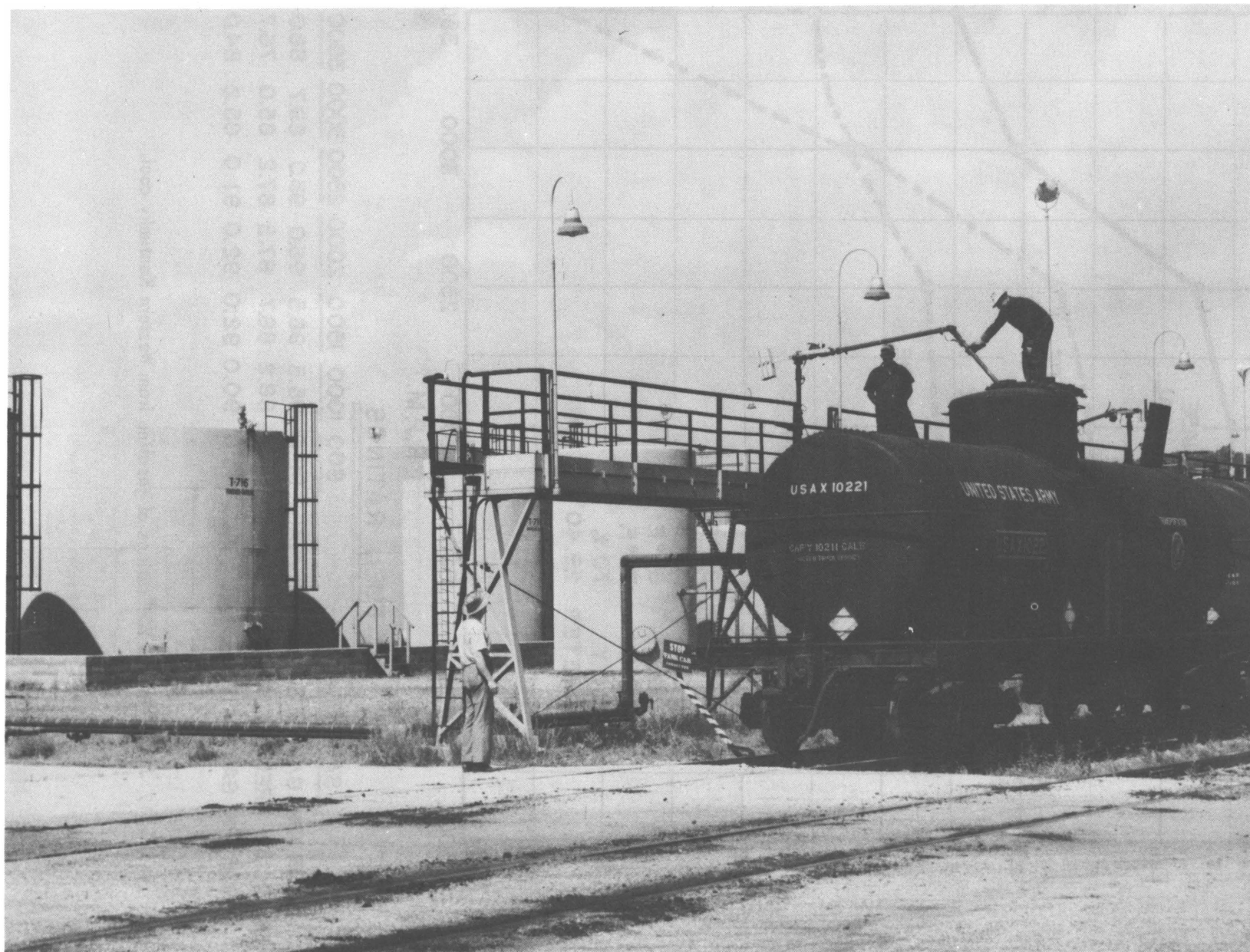
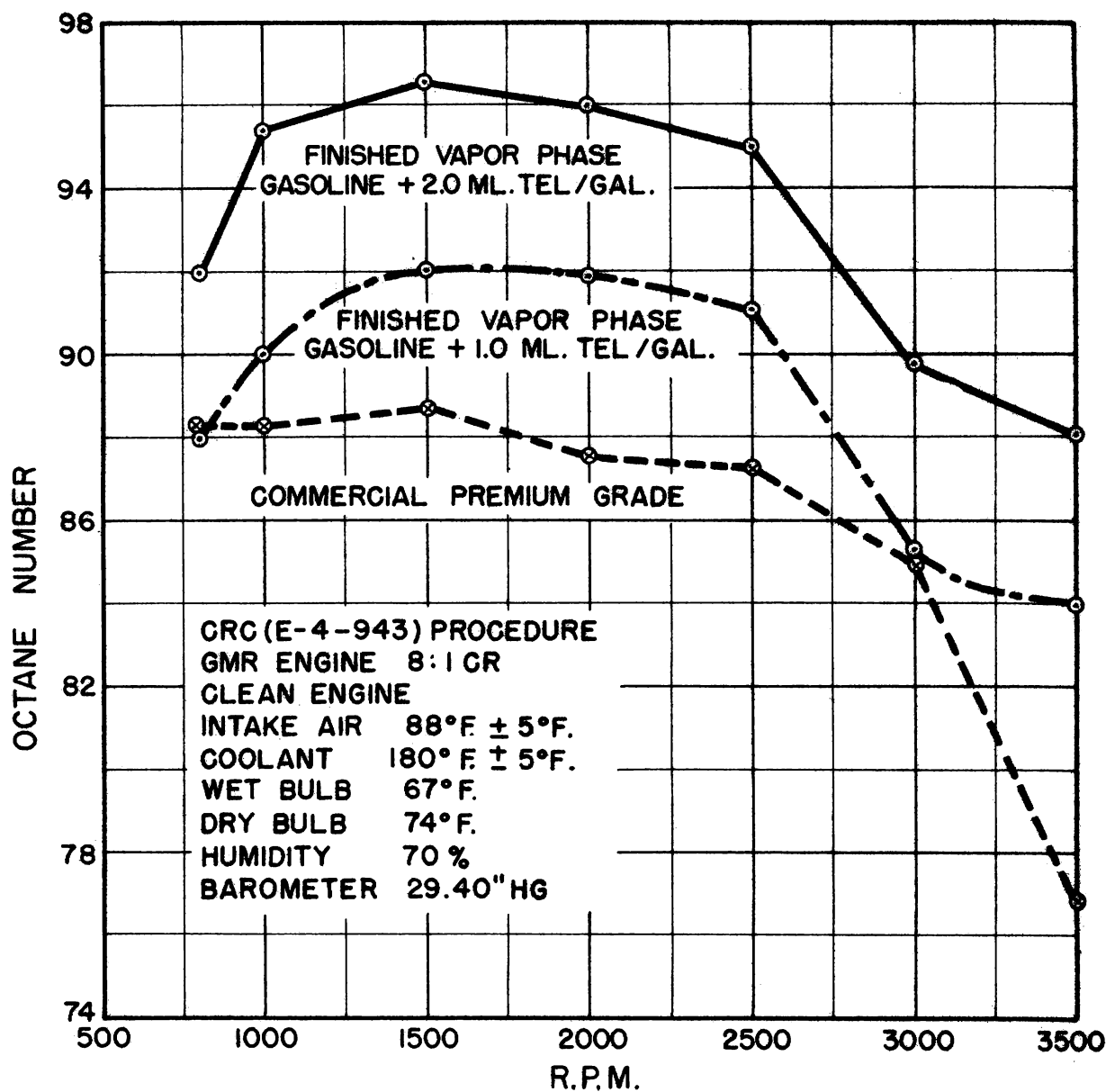


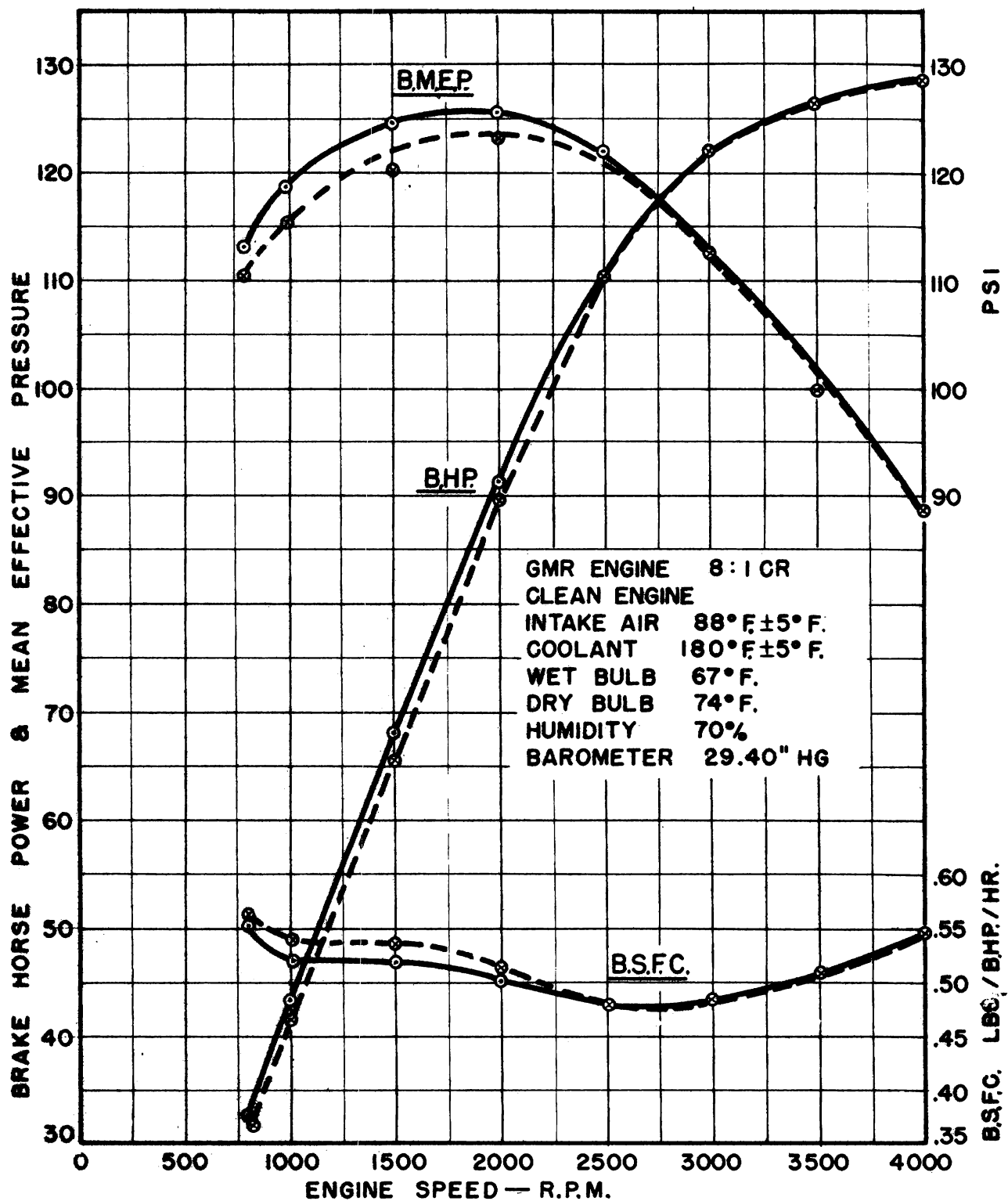
Figure 11. - Loading gasoline made from Rock Springs coal for shipment to Army.



FUEL RATINGS

<u>SAMPLE</u>	<u>800</u>	<u>1000</u>	<u>1500</u>	<u>2000</u>	<u>2500</u>	<u>3000</u>	<u>3500</u>
FIN. VAPOR PH. GASO. +2.0 ML. TEL./GAL.	92.0	95.5	96.5	96.0	95.0	89.7	88.0
COMMERCIAL PREMIUM GRADE	88.2	88.2	88.7	87.5	87.2	85.0	76.7
FIN. VAPOR PH. GASO. +1.0 ML. TEL./GAL.	88.0	90.0	92.0	92.0	91.0	85.2	84.0

Figure 12. - Dynamometer fuel ratings of gasoline from Western Kentucky coal.



○ — FINISHED VAPOR-PHASE GASOLINE + 2.0 ML. TEL
 ● — COMMERCIAL PREMIUM GAS

Figure 13. - Maximum performance curves, knock limited, for gasoline from Western Kentucky coal.
 B.M.E.P. is brake mean effective pressure, B.H.P. to brake horsepower, and B.S.F.C. to best-setting fuel consumption.

Lead susceptibility

	<u>Octane No.</u>			
	Western Kentucky Motor	Research	Rock Springs Motor	Research
Gasoline + 1 ml. TEL/gal.	84.2	90.8	82.6	88.6
Gasoline + 2 ml. TEL/gal.	86.8	93.7	85.7	92.5
Gasoline + 3 ml. TEL/gal.	88.9	96.2	88.4	94.3

It is evident that both of these fuels have good lead-susceptibility characteristics and meet the requirements for a high-quality gasoline.

The finished vapor-phase gasoline from Western Kentucky No. 11-bed coal was subjected to dynamometer tests made on a General Motors research engine at 8:1 compression ratio to determine its maximum performance characteristics and octane ratings. A conventional commercial-type premium-grade gasoline was run for comparative purposes. The CRC designation E-4-943 test procedure was used to determine the fuel ratings. The maximum performance characteristics were developed at full throttle, and the spark timing was adjusted for trace knock or peak power, depending upon the detonation tendency of the fuel. The results are summarized in figures 12 and 13.

Examination of the curves indicates that the vapor-phase gasoline has a higher octane rating than a commercial-type premium fuel. The brake horsepower and mean effective pressures developed by the vapor-phase gasoline with 2 cc. per gallon TEL added were higher than the premium fuel at engine speeds below 2,500 r.p.m. and the same at 2,500 r.p.m. and higher. The fuel consumption was likewise lower at the lower speeds and the same at 2,500 r.p.m. and higher. This can be attributed to the fact that both fuels satisfied the maximum power octane-number requirement at the higher engine speeds.

Aviation-Base Gasoline

The sample of aviation-base gasoline produced from Western Kentucky No. 11-bed coal had the following properties:

Gravity	°A.P.I.	54.0
Distillation:		
10 percent evaporated	°F.	155
50 percent evaporated	do.	209
90 percent evaporated	do.	277
E.B.P.	do.	324
Recovery	percent	99.0
Residue	do.	1.0
Sum of 10 percent and 50 percent evaporated	°F.	364
Acidity of distillation residue		Nil
Vapor pressure	p.s.i.	5.6
Corrosion, copper strip		Negative
Copper dish gum	mg./100 ml.	12.5
Potential gum	do.	2.4
Sulfur content	percent	0.03
Freezing point	°F.	2 below 0
Water tolerance		Immiscible
Aniline point	°F.	87.8
Heat of combustion	calculated B.t.u./lb.	18,710
Octane number:		
Lean mixture		75.2
Performance number		53.
Rich mixture		Too low for use of method

This gasoline was blended with isopentane and alkylate and the blends tested for meeting the requirements for 91/98, 100/130, and 115/145 gasolines. The compositions and vapor pressures of the blends were as follows:

<u>Blend</u>	<u>91/98</u>	<u>100/130</u>	<u>115/145</u>
Aviation-base gasoline percent	88.9	53.3	19.6
Isopentane do.	11.1	6.7	2.4
Alkylate do.	-	40.0	78.0
TEL ml./gal.	4.6	4.6	4.6
Vapor pressure p.s.i.	7.0	6.7	6.7

The results of the tests are as follows:

<u>Blend</u>	<u>Lean mixture</u> <u>(A.S.T.M.-D 614-49T.)</u>	<u>Rich mixture</u> <u>(A.S.T.M.-D 909-48T.)</u>
91/98		
Octane rating	92.7	Iso-octane plus 0.37 ml. TEL/gal. 112.5
Performance No.	-	
100/130		
Octane rating	99.9	Iso-octane plus 1.55 ml. TEL/gal. 133.5
Performance No.	-	
115/130		
Performance No.	Iso-octane plus 0.47 ml. TEL/gal. 115	Iso-octane plus 3.0 ml. TEL/gal. 146.6
Alkylate		
Performance No.	Iso-octane plus 0.98 ml. TEL/gal. 125.4	Iso-octane plus 4.6 ml. TEL/gal. 155.5

Results of these tests indicate that the base stock, after blending, meets the knock-value requirements for all grades of aviation gasolines. Except for the copper-dish gum and freezing points, the fuel meets all inspection tests outlined in A.S.T.M.-D 910-48T. The copper-dish gum is only slightly high, but the freezing point is much too high. The freezing-point specification was easily met in German plants processing bituminous coal. Investigations in the Bureau's laboratory show that our gasoline has a freezing point of -70° F. The cause of the discrepancy between the Bureau and commercial laboratory determinations of freezing point is not yet known but is being investigated.

Jet Fuel

A sample of jet fuel made from vapor-phase products obtained by hydrogenation of Western Kentucky No. 11-bed coal also was tested. The blend contained 25 percent vapor-phase distillation bottoms, 40 percent aviation-base gasoline, and 35 percent finished vapor-phase gasoline.

The results of the laboratory tests were as follows:

Gravity	°A.P.I.	45.4
Distillation:		
10 percent evaporated	°F.	158
50 percent evaporated	do.	255
90 percent evaporated	do.	432
End point	do.	557
Recovery	percent	99.0
Residue	do.	1.0
Reid vapor pressure	p.s.i.	6.1
Freezing point	°F.	2
Corrosion, ("air-well" copper strip)		No evidence
Existent gum	mg./100 ml.	13.8
Accelerated gum	mg./100 ml. (16 hrs.)	15.8
Aromatics	percent	26.6
Sulfur	do.	0.024
Water tolerance		Immiscible
Bromine number		16
Heat of combustion	B.t.u./lb. (calculated)	18,520

The blend meets specification MIL-F-5624A, except the aromatics limitation of 25 percent and the freezing point, -76° F. The earlier comments also apply in this case.

Chemicals

Routine laboratory determinations have been made of the total contents of the chemicals under discussion in the product streams from three coals. These contents, as volume percent of product streams, are given in table 3 for the liquid-phase operations and in table 5 for the vapor-phase. Liquid-phase tar acid and base percentages are given for Rock Springs, Western Kentucky, and Illinois coals and aromatics for the last two coals only, as these determinations were not made during the Rock Springs liquid-phase runs. Vapor-phase percentages for the three types of chemicals are given for Rock Springs and Western Kentucky coals only, as the Illinois liquid-phase product has not yet been processed in vapor-phase.

The difference in content of chemicals in the respective liquid-phase streams of the three coals may be attributed to several factors, such as:

- (1) Difference in boiling range of the respective streams for each coal;
- (2) type of catalyst used in processing; (3) severity of processing; and
- (4) inherent differences in the coals themselves. The Rock Springs coal was processed with tin catalyst and subjected to a severe treatment, as attested in table 2 by the high reaction temperatures and the negative yields in heavy oil. Western Kentucky and Illinois coals were processed under milder conditions - Illinois entirely under FeSO_4 as catalyst and Western Kentucky with tin, tin and iron, and finally with iron as FeSO_4 .

The total content of the three type chemicals in the liquid-phase light oils is given in table 6 in pounds and in gallons per ton of moisture- and ash-free coal processed. It may be significant that the gross contents of tar acids are lower for both coals with which tin catalyst was used. However, the processing severity for the Rock Springs coal must not be overlooked, and

it appears that the high temperatures to which this coal was subjected, though bringing about high reduction of tar acids, at the same time may have caused retention of a higher degree of aromaticity.

The gross content of the lower-boiling tar acids ($<225^{\circ}\text{C.}$), which constitute the bulk of industrial demand, is given in table 7 for the three coals. These values are based on analyses by the Synthetic Liquid Fuels Research Branch at Bruceton, Pa., from liquid-phase light-oil blends derived from these coals. The higher yields of phenol and cresols from Western Kentucky and Illinois coals are evident at once. However, the blends represent yields under processing conditions attained at this plant only and must not be interpreted as the maximum yields possible.

TABLE 6. - Gross contents of tar acids, tar bases, and aromatics in liquid-phase light oils

Based on m.a.f. coal processed	Rock Springs		Western Kentucky		Illinois	
	Gal./ton coal	Lb./ton coal	Gal./ton coal	Lb./ton coal	Gal./ton coal	Lb./ton coal
<u>Tar acids</u>						
Gasoline	2.4	21.2	0.9	7.6	0.1	0.9
Naphtha	(1)	(1)	13.9	117.1	17.4	146.5
Middle oil ...	20.3	175.9	13.4	116.6	18.4	159.2
Total	22.7	197.1	28.2	241.3	35.9	306.6
<u>Tar bases</u>						
Gasoline	1.5		0.6		0.3	
Naphtha	(1)		.3		.2	
Middle oil ...	2.5		.1		Negligible	
Total	4.0		1.0		.5	
<u>Aromatics</u>						
Gasoline	No individual stream analysis available		6.4		4.1	
Naphtha			11.9		17.9	
Middle oil ...			27.6		42.4	
Total	65.6		45.9		64.4	

1/ Naphtha included in gasoline and middle oil.

TABLE 7. - Gross content of low-boiling tar acids in liquid-phase light oils

Based on m.a.f. coal	Rock Springs		Western Kentucky		Illinois	
	Gal./ton coal	Lb./ton coal	Gal./ton coal	Lb./ton coal	Gal./ton coal	Lb./ton coal
Phenol	2.5	22.4	3.1	27.4	2.8	24.7
o-Cresol	1.1	9.6	0.7	6.2	1.1	9.4
m-Cresol	2.4	21.2	2.3	20.1	2.8	24.1
p-Cresol	0.7	6.4	1.2	10.3	1.4	11.8
Subtotal	6.7	59.6	7.3	64.0	8.1	70.0
Mixed xylenols	4.6	39.8	-	-	-	-
Total	11.3	99.4	-	-	-	-

The gross chemical contents of vapor-phase gasolines derived by processing the liquid-phase light oil from Rock Springs and Western Kentucky coals are given in table 8. Comparison of this table with table 6 for the liquid-phase streams at once makes evident the reduction in tar acids that takes place during the vapor-phase processing. The aromatic content on a volume basis compares favorably with the quantities in the feed. Furthermore, a molecular reduction takes place during the vapor-phase processing, converting the heavier aromatics into low-boiling aromatic gasoline components that improve the fuel properties of gasoline or may be separated for industrial usage. Conversion of heavier-boiling compounds by vapor-phase processing into industrially usable low-boiling aromatics is illustrated in the first two columns of table 9 that compare the content of the various compounds in the 50° to 150° C. fractions of liquid- and vapor-phase gasolines from Rock Springs coal. These values are given in pounds per ton of moisture- and ash-free coal processed and again are based on analyses furnished by the Synthetic Fuels Research Branch at Bruceton. Not only do the low-boiling aromatic yields increase tremendously on destructive hydrogenation of the liquid-phase light oils, but also there is a comparative increase in aromatic materials that may be converted by industrial catalytic aromatization processes.

To determine the effectiveness of industrial processes in the aromatic enrichment of coal-hydrogenation gasolines, cooperative study agreements have been made with Universal Oil Products and the Standard Oil Co. of Indiana, wherein gasolines from the demonstration plant have been subjected to plat-forming and hydroforming under various degrees of treatment severity. The results of these cooperative tests will be published as a joint report. Both processes appear quite suitable for processing final coal-hydrogenation gasolines from the vapor phase.

Column 3 of table 9 gives the indicated yields of the various hydrocarbons had the vapor-phase 50° to 150° C. product been subjected to catalytic aromatic enrichment. A study of aromatic enrichment of liquid-phase gasoline by hydroforming is now in progress.

TABLE 8. - Gross contents of tar acids, tar bases and aromatics in vapor-phase raw gasoline

	Rock Springs		Western Kentucky	
	Gal./ton coal	Lb./ton coal	Gal./ton coal	Lb./ton coal
Tar acids	0.7	6.0	1.0	8.7
Tar bases	1.0	-	1.0	-
Aromatics	43.4	-	37.6	-

TABLE 9. - Comparison of contents of various components in 50° - 150° C. cuts of liquid- and vapor-phase gasoline from Rock Springs coal

Components in 50° - 150° cuts	Pounds per ton of coal		
	Liquid phase	Vapor phase	Vapor-phase cat. aromatized ^{1/}
Paraffins, total	27.6	143.5	98.8
Naphthenes, total	71.4	384.0	91.2
Cyclopentane	0.3	2.6	2.1
Methylcyclopentane	3.6	64.6	37.9
Cyclohexane	10.8	26.6	5.1
Dimethylcyclopentanes	4.5	53.2	22.9
Methylcyclohexane	12.7	52.7	6.8
Ethylcyclopentane	4.8	38.9	4.4
C ₈ - Naphthenes)	17.5	78.3	12.9
C ₉ - Naphthenes)	10.5	67.2	
Aromatic, total	33.5	208.7	412.0
Benzene	2.5	46.1	86.8
Toluene	11.0	83.3	158.3
Ethylbenzene	11.6	23.7	47.4
m-p-Xylene	5.3	46.8	95.8
o-Xylene	2.9	8.8	22.9
Olefins, total	15.2	8.3	13.7
Total	147.7	744.5	614.9
Nonhydrocarbons, total	11.3	10.6	

^{1/} Probable yields had the vapor-phase cut been subjected to catalytic aromatization. Estimates based by the Bureau on results obtained by the Standard Oil Co. of Indiana upon hydroforming of vapor-phase gasoline through a cooperative agreement. Full results of cooperative work will be published later.

Gas-Synthesis Demonstration Plant

Coal Gasification

Installation of the new Morgantown-type vertical oxygen-coal gasifier (fig. 14), described in the 1950 Annual Report, has been completed. A flow diagram of this system, which employs a new method of feeding preheated steam-coal mixtures, is shown as figure 15. Existing equipment was used as far as possible in the hook-up.

The coal-feeding system consists of accumulator metering tanks for coal and water, which dump periodically into a slurry-mix tank as additional material is required in the latter. This tank is equipped with two high-speed, propeller-type agitators and is of 1,600 gallons capacity, large enough to

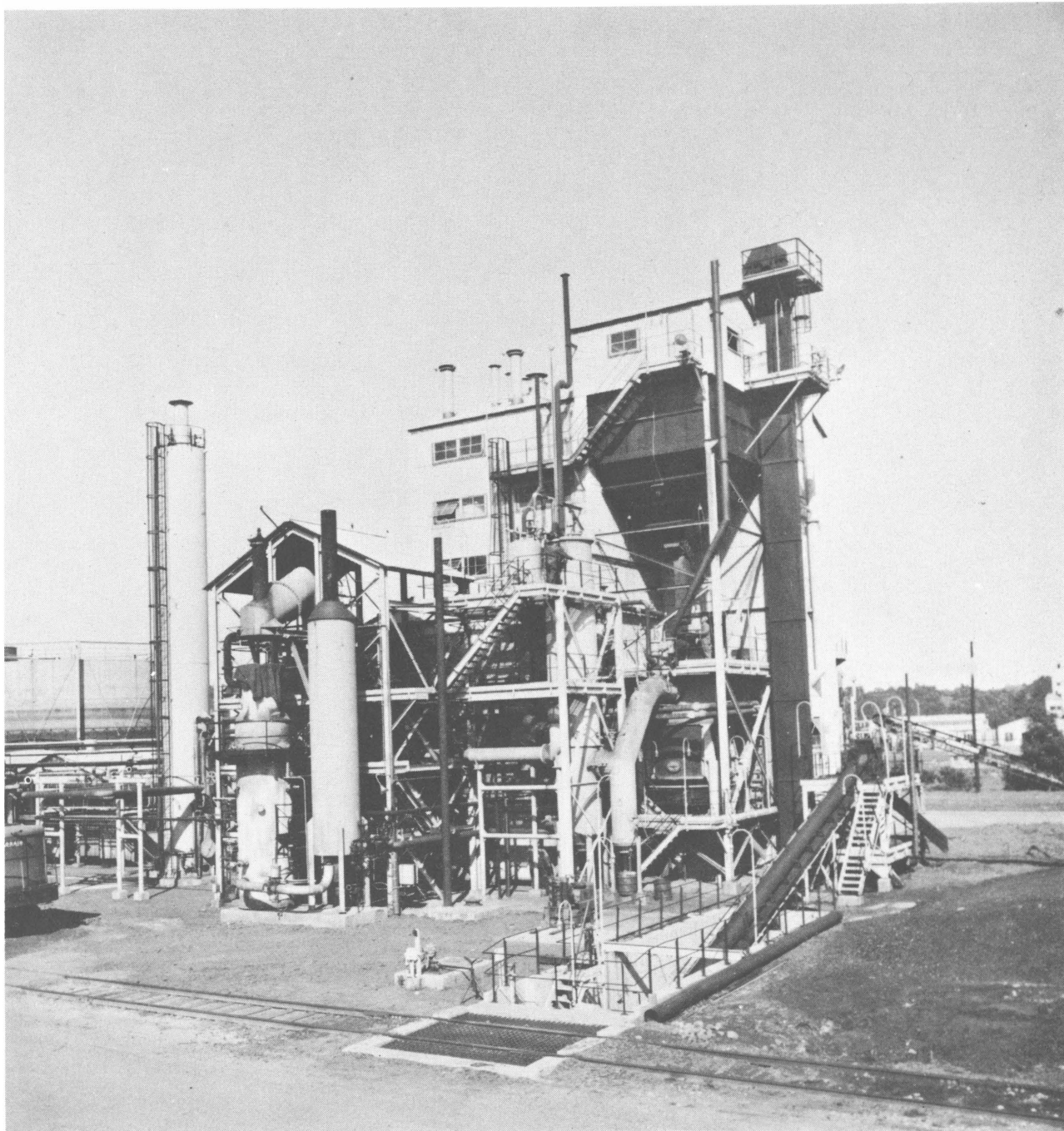


Figure 14. - Coal-Gasification Unit. On right is Kerpely coke gasification unit, on left next to tall washer-cooler is Morgantown-type vertical gasifier and steam superheater.

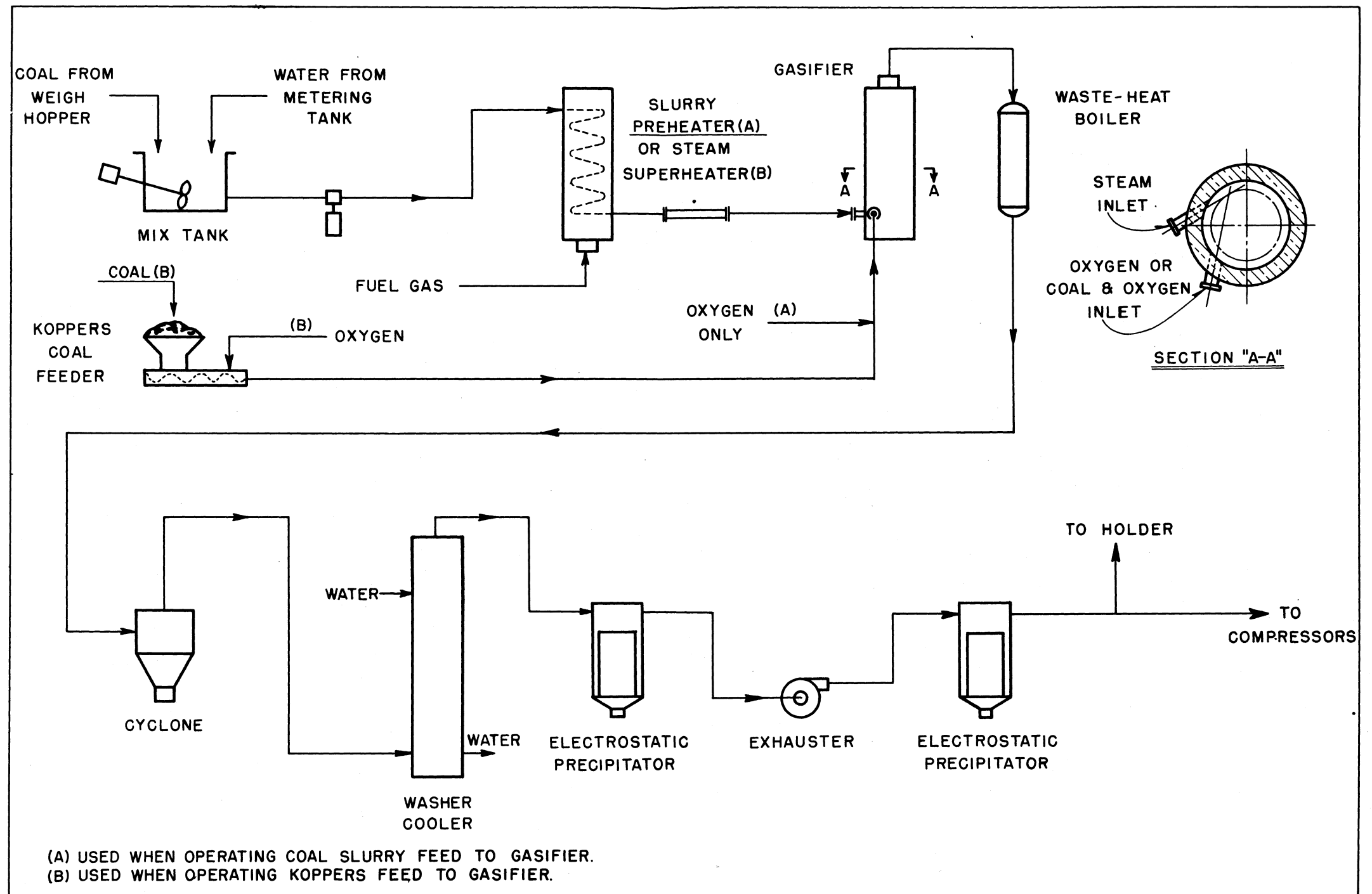


Figure 15. - Schematic flow diagram - gasification.

provide several hours' operation and minimize any changes in concentration owing to intermittent dumping. The discharge line from this tank is about 6 inches above the bottom of the tank and is connected to the suction of a reciprocating pump, motor-driven through a variable-speed oil gear. The pump discharge enters the top of a fired coil in which the water is vaporized, and the resulting steam-coal mixture is superheated to 900° to 1,000°F. The coil consists of a preheater section of several turns of 3/4-inch pipe, followed by an evaporating section of 2-inch pipe, which, in turn, leads into the superheating section, made of 3-inch, 4-6 chrome tubing. The transfer line from the coil discharge to the gasifier was kept as short as possible and is heavily insulated. The heated steam-coal mixture was introduced into the gasifier about 1-1/2 feet above the bottom and tangent to a circle of slightly smaller diameter than the gasifier itself. Oxygen is brought in through another nozzle at the same level and tangent to the same inner circle. The gasifier proper consists of a vertical refractory-lined cylinder, 4 feet, 4 inches, inside diameter and approximately 20 feet in height. Provision was made for measuring temperatures and pressures throughout the length of the unit. The refractory is high-purity aluminum oxide that was ram-packed against inside forms and fired in place to produce a monolithic lining. This material has the advantage of higher melting point and much higher resistance to thermal shock than the silica brick used in the previous unit. If tests here show that the monolithic lining is satisfactory, important economies in construction costs may result. Under a cooperative agreement, the Aluminum Co. of America supplied much valuable technical assistance and the major part of the material.

Products from the gasifier pass out the top and into the same waste-heat boiler and gas-handling system that were used with the previous gasifier - that is, a cyclone dust catcher, gas-washer cooler, electrostatic dust precipitators, and gas exhauster.

To test operation of the coal slurry-feed system independent of the gasifier operation, the connection between the slurry preheater and gasifier was removed so that the material leaving the preheater coil would discharge into the air and its characteristics could be observed. On the first tests, there was some trouble with plugging of the coil, and the discharge stream was quite erratic, alternately blowing almost clear steam and very dense clouds of coal dust. An orifice then was installed in the discharge line to hold a back pressure of about 15 pounds on the coil, and the uniformity of discharge seemed definitely improved but still unsatisfactory. A smaller orifice was installed, which gave a back pressure of about 40 pounds, and a further improvement was noted, although it was felt that the stream still was not uniform enough to warrant use as a gasifier feed. Further increases in pressure could not be made on this coil without exceeding its safe working pressure at the temperatures encountered.

Pumping difficulties occasionally had been encountered and in every instance a small amount of very coarse coal particles was found under the pump valves. To eliminate this, a vibrating "scalper" screen was installed in the coal-pulverizing system to remove the +30-mesh material.

At this point the necessity for determining the operability of the gasifier proper led to the decision to postpone further work on the slurry feed and adapt one set of Koppers screw feeders to use on this new unit. The slurry feed heater was used as a steam generator and superheater.

The slurry method of feeding, if successful, would have its greatest advantage in connection with a gasification unit operating under elevated pressures. Plans are now in progress for a new coil designed to operate at appreciably higher discharge pressures. If this higher pressure makes the operation satisfactory, the unit as constructed will be suitable for use when a demonstration-scale pressure-gasification unit is installed. Until that time it can be used as feed for a gasifier operating at atmospheric pressure.

Tests on New Gasification Unit

Several runs have been made in the vertical gasifier, and the results of four were reliable enough to warrant calculation. Best results were achieved in a 3-day run with the unit on stream about 70 percent of the time. Owing to difficulty with the coal feed screws, the oxygen:coal ratio was above that planned, and ranged between 11 and 12 cubic feet of oxygen per pound. Carbon conversion was 97 to 99.5 percent. All of the stable operating periods and the average of the whole run were appreciably better than any results obtained on the previous unit, and the results of the best period of operation closely approach those achieved in the Morgantown vertical pilot-plant unit on this same coal.

During this run there was evidence that deposition of slag in front of the burner nozzle deflected the oxygen-coal flame so that it impinged directly on the lining. As a result of local high temperatures, a considerable portion of the alumina was melted out, and the run was ended with 12 to 15 inches of an extremely hard, high-melting mixture of aluminum oxide and coal slag in the bottom of the gasifier.

After this run, it was felt that a change in the oxygen-coal nozzle to make it tangent to a smaller circle would help prevent the build-up of slag deposits from the wall to the point where it could block the oxygen-coal stream. Examination of the gasifier after the run indicated that the main path of the superheated steam was below that of the oxygen-coal stream within the gasifier and that better mixing would be achieved if the steam were directed slightly upward. A new steam nozzle was installed to achieve this. The crater from which the alumina had been melted was patched with small, pre-fired alumina shapes, cemented in place by an alumina ram mix.

Two runs were made after these changes; the results were definitely inferior to those of the preceding run and little if any superior to those achieved on the Koppers gasifier. Inspection of the unit after these runs showed no evidence of damage to the refractory, either from melting or erosion. Present efforts are directed toward further changes that will protect against damage to the refractory and still permit the efficient operation previously achieved.

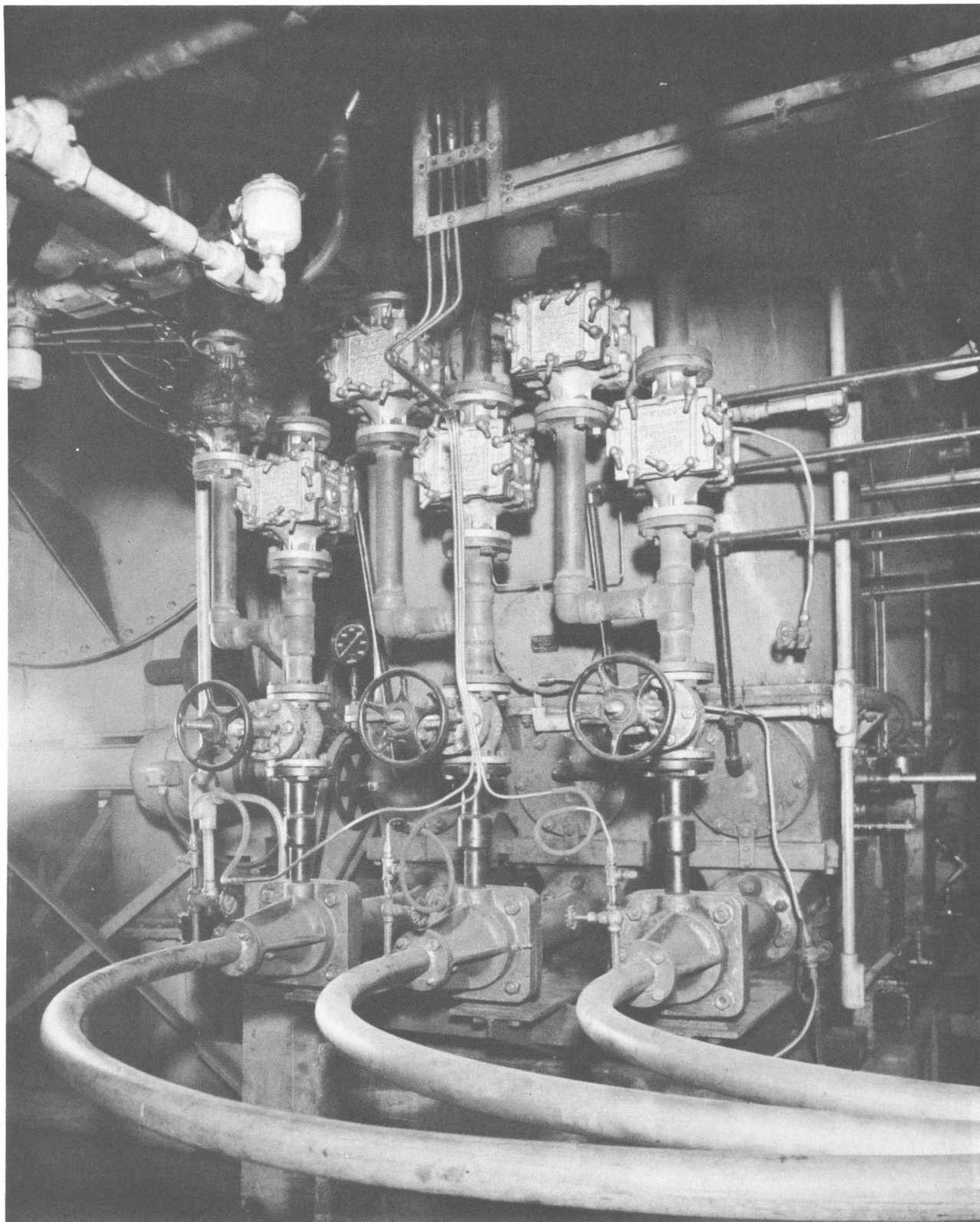


Figure 16. • Pulverized-coal screw feeders and coal-transfer tubes in coal-gasification unit.

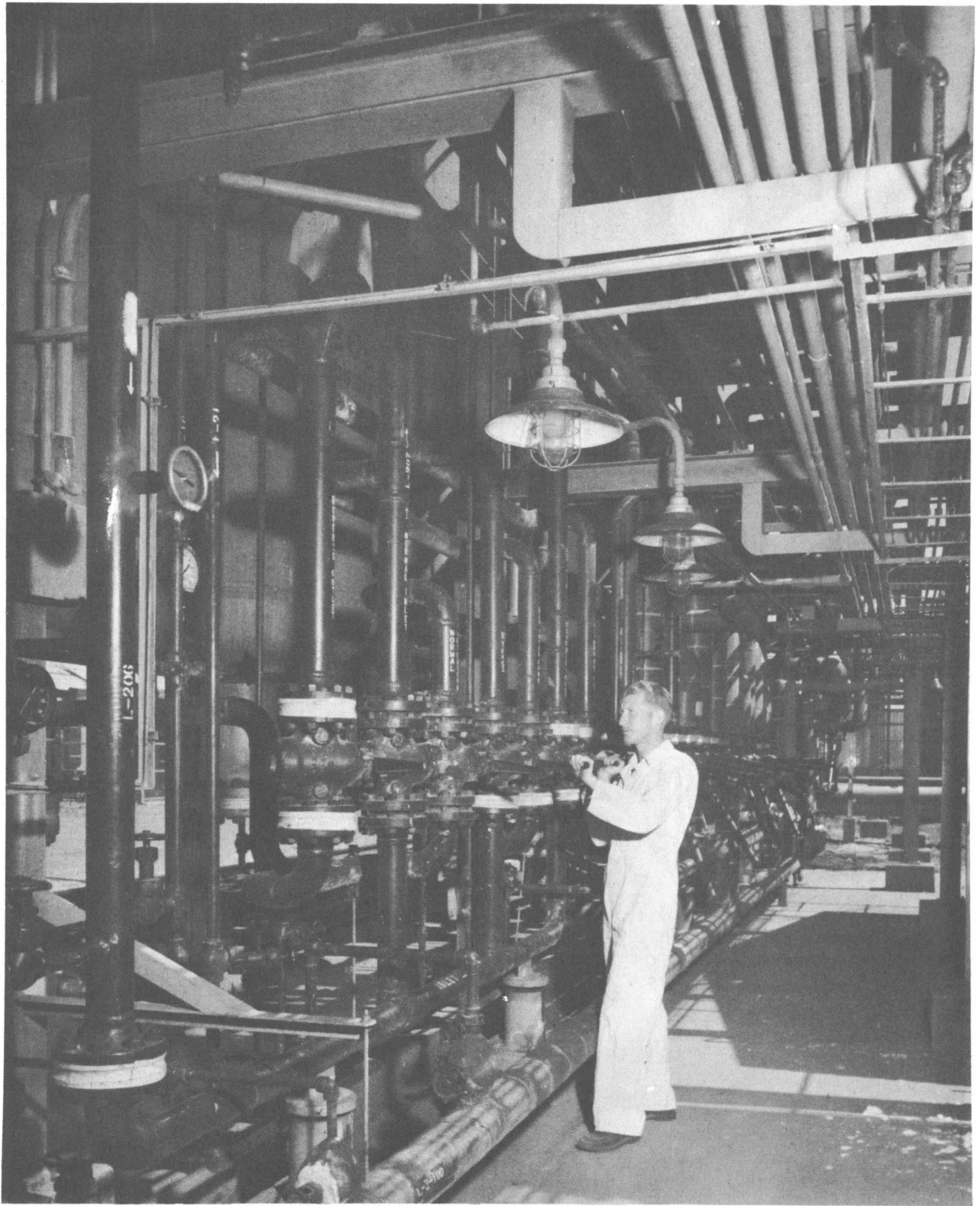


Figure 17. - Piping and manifold in gas-purification unit that removes sulfide from synthesis-gas stream.

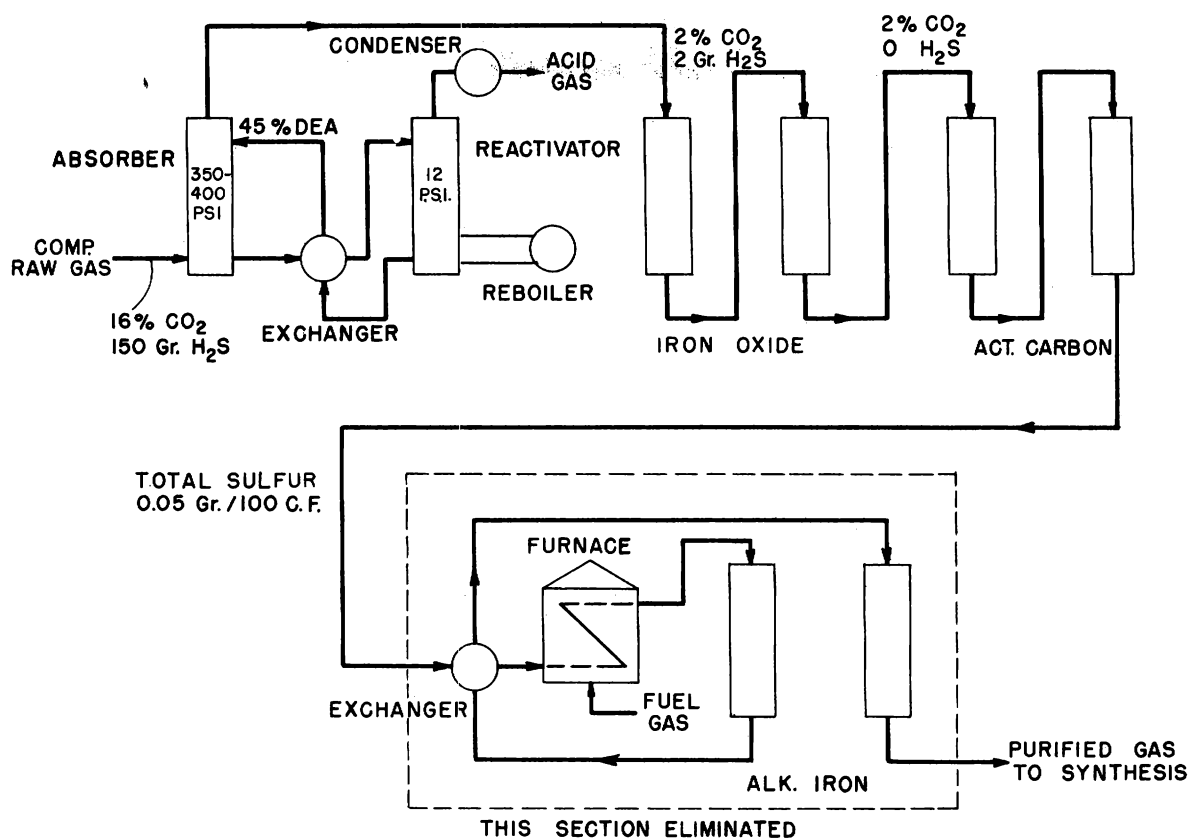


Figure 18. - Schematic flow diagram - synthesis-gas purification.

Further work on this unit was postponed to test and put into operation the gas-purification section of the plant, in preparation for the forthcoming synthesis run. In testing the purification unit, the Kerpely producer, using oxygen, coke, and steam, was employed as a source of synthesis gas and was operated for several extended periods. Between May and November 1951, the producer was in operation for a total of about 1,400 hours. During this time 23,000 M standard cubic feet of process oxygen and 1,450 tons of coke were fed, producing 113,000 thousand standard cubic feet (M std. cu. ft.) of make gas. The gas produced normally is of the following composition:

CO ₂	percent	16
H ₂	do.	36
CO	do.	46
H ₂ S	grains per 100 cu. ft.	150

On an over-all basis, these production figures indicate a requirement of 30.8 pounds of coke as charged and 243 standard cubic feet of oxygen (100 percent) per thousand cubic feet of CO + H₂. This compares very favorably with the published reports of commercial oxygen-blown producers.

In the operations during September and October 1951, about 45 million cubic feet of gas was produced and about 40 million cubic feet purified. A substantial part of the purified gas produced during these later operating periods was used as feed for the Fischer-Tropsch synthesis unit.

Operation of the producer and its auxiliaries, although not entirely trouble-free, has been quite steady and reliable. Some trouble was encountered with deposits of very heavy tar in the gas exhauster. As originally installed, there were two electrostatic precipitators in series between the exhauster and the gas compressors to remove dust from the compressor feed gas. Piping was changed to put one of these precipitators in the gas line leading to the exhauster. This almost completely eliminated the tar deposits in the exhauster, and the single precipitator in the compressor feed line was adequate to remove dust and tar.

Operation of Purification Unit

The problem of purifying synthesis gas is one that has been given a great deal of study. The tolerance of the Fischer-Tropsch catalysts for sulfur compounds is extremely low, and it had been hoped to produce a gas containing not more than 0.1 grain of sulfur per 100 cubic feet. Later, bench-scale and pilot-plant studies on the synthesis indicated that carbon dioxide also should be as low as possible. A photograph and a flow diagram of the purification system as originally installed are shown in figures 17 and 18. The cleaned gas is compressed to synthesis operating pressure and scrubbed to remove carbon dioxide and hydrogen sulfide with a 35- to 45-percent solution of diethanolamine in water. Used diethanolamine is expanded to about 12 pounds pressure and sent to a reactivator wherein the combined action of decreased pressure, heat, and water vapor removes the absorbed carbon dioxide and hydrogen sulfide, which then are vented to the flare stack. The revived diethanolamine is cooled and pumped back to the absorber. Synthesis gas leaving the absorber contains only about 2 percent of carbon dioxide and 1 to 2 grains of hydrogen

sulfide per 100 cubic feet. It is passed downward in series through two beds of iron oxide on wood shavings, which remove completely the residual hydrogen sulfide. To remove the organic sulfur compounds, the gas next is passed downward through two beds in series filled with active carbon. This material has the property of adsorbing and retaining the organic sulfur compounds. When the carbon in one bed becomes saturated, it is removed from the line and regenerated by blowing with superheated steam. Then it is returned to service as the second bed.

Almost without exception, in German synthetic-fuel operations, beds of hot iron oxide-soda ash mixture were employed as a final purification measure. This material decomposed the organic sulfur compounds which passed the active carbon and absorbed the hydrogen sulfide formed. As a precaution, similar beds were included in the design of the Louisiana purification system. It should be noted, however, that the German purification plants operated under substantially atmospheric pressure. In the laboratory-scale purification work at Morgantown, W. Va., it was found that the active carbon would remove organic sulfur completely when operated 300 to 400 p.s.i., so that it was generally felt that the iron oxide-soda ash mixtures were not necessary. Also, economic calculations had shown that removal of organic sulfur by active carbon was very much cheaper than by the German system.

Mechanical operation of the purification unit was tested, and the preliminary operator training was accomplished by "dummy" runs in which inert gas was used instead of synthesis gas. After a short period of such operation, the purification unit was first put into service from May 29 to June 8, 1951, on gas made in the Kerpely producer. There were, of course, many operating difficulties and disappointments, but even in this first period it was rather clearly demonstrated that the gas ultimately could be purified to the degree required for the synthesis unit. Since this first trial, there have been four major periods of operation, each more reliable and more satisfactory than the preceding one. During one of the early operations, considerable trouble was experienced with the iron oxide-soda ash mixtures. It was found that, during operation under these elevated pressures, particularly with traces of oxygen present in the gas, undesirable side reactions were promoted that led to release of heat and very difficult temperature control. In one instance this resulted in overheating until the vessel wall failed. In view of the substantially complete removal of organic sulfur by active carbon under the operating conditions, it was decided that the iron oxide-soda ash mixture was unnecessary and undesirable, and the piping has been changed to eliminate it from the system.

In the last two periods 40,000 thousand cubic feet of gas was processed, during a total operating time of 540 hours. In present operations, the feed gas to the synthesis unit consistently contains less than 2 percent carbon dioxide, and the total sulfur content in general is well below 0.05 grain per 100 cubic feet.

As the gas from the Kerpely producer is similar in composition and character of impurities, it is felt that the present operation gives full assurance that the gas from any high-temperature coal-gasification unit can be purified

to the extent required for the Fischer-Tropsch synthesis. Work is to be continued on this unit to improve the operating efficiency and reduce the cost of the purification step.

Operation of Oxygen Plant

The oxygen plant continued in operation as required for the coal-gasification experiments and later for the Kerpely producer. To November 1, the plant had operated 3,000 hours during the year and produced 60 million cubic feet of product oxygen. Only twice have there been unplanned interruptions to the oxygen-plant operation. In one, a German motor on the low-pressure compressor failed in the windings. A new motor was procured, and the German motor was rewound to serve as a spare. Later a bearing on the new motor overheated badly, and the rewound German motor was reinstalled, with a total interruption to oxygen production of only 10 hours. During this time the purification and synthesis plants operated with reduced throughput from the storage holder, so that no shutdown was necessary.

Theoretical Studies

The thermodynamic studies of coal gasification mentioned in previous reports have been extended to cover substantially all probable operating conditions. These studies determine what theoretically may be obtained from a given coal under specific conditions but do not give information as to the effect of time, temperature, and pressure on the relative speed and degree of completion of the various reactions involved. Because of the complex nature of coal, the high temperatures involved, and the important effect of heat losses on results, basic laboratory research on this problem is extremely difficult.

It was felt that a mathematical attack on this problem, using what fundamental information is available, and later comparison of calculated with actual operating results might be a more feasible approach.

After a study of published information, the basic assumptions were formulated and work started on a method of calculation. Each small-time increment involves a change in the temperatures, composition of the reaction mixture, the particle size of the coal, and many other factors. Because of the many variables and the complexity of the calculations, it was found that about 64,000 computations are required to solve a single case involving a single set of operating conditions.

Fortunately the equations could be cast in a form that would make possible the use of the International Business Machine (I.B.M.) sequence calculator used by the Explosives and Physical Sciences Division at Pittsburgh. This machine will make the 64,000 calculations in 6 hours' operating time. The actual computation work was begun near the end of the year. Twenty cases will be calculated, covering variations in oxygen:coal and steam:coal ratios at various temperatures.

After this work is completed, it should be possible to study the theoretical effect of these changes upon the progress of the various reactions involved. Comparison of these results with those of actual operation of the gasifier at Louisiana and others then should lead to a better understanding of the real effect of these variables and point the way to the most efficient operation.

Making and Reducing Catalyst for Synthesis Operations

The catalyst fusion unit (see fig. 19) was described briefly in the 1950 Annual Report. The process for manufacturing synthetic ammonia-type fused iron oxide catalyst was novel in two respects. First, a commercial mill scale, economical and readily obtainable from steel rolling mills, was employed as the base material in place of magnetic iron oxide from the combustion of iron in oxygen, which had been used in the past. The mill scale was found to be pure enough for the purpose, although the ferrous:ferric iron ratio varied somewhat from a pure magnetic iron oxide. Secondly, the ferrous:ferric iron ratio was adjusted in the treatment, so that the proper ratio was obtained in the finished catalyst.

In 1951, 75,800 pounds of sized, unreduced catalyst was produced at a cost of \$0.16 per pound. This cost does not include amortization of the plant but includes all other known elements of cost, such as materials, labor, utilities, and miscellaneous expense.

The catalyst-reduction unit was tested thoroughly in preliminary operations with sized sand approximating the size of the catalyst, and the apparent operational difficulties were determined and corrected. A total of 27,800 pounds of reduced catalyst was made.

Some difficulties were experienced in early operation of the catalyst-reduction unit. One of the most serious was deposition of carbon on screens and within the body of catalyst undergoing reduction. This was due to reduction of carbon-containing compounds in the hydrogen and was corrected by passing the heated hydrogen over a methanating catalyst before passage through the catalyst in the reduction vessel. A second serious difficulty was the channeling of catalyst in the reduction vessel. The reduction procedure was changed from continuous to batch operation, and from then on no further serious difficulties were experienced. The earliest catalyst processed in this operation was reduced to about 70 percent iron, while the balance was reduced to 85 to 95 percent.

Tests on the catalyst in bench-scale, pilot-plant, and demonstration-plant operations have shown this material to be as satisfactory as any other catalyst previously tested.

Fischer-Tropsch Synthesis and Distillation

Before the synthesis and distillation units were tested, several important changes were made. These included revisions to piping and equipment and correction of mechanical difficulties that affected the performance of several of the pumps and control instruments. In addition, insulation of exposed lines and equipment was completed.

In the synthesis unit the most important change adapted the synthesis reactor for "jiggling-bed" operation. Originally the synthesis reactor, 6 feet in diameter by approximately 30 feet over-all (see fig. 20), was designed for fixed-bed operation as an internally cooled converter. Because the "jiggling-bed" process requires the coolant oil and gas flows to be within defined linear

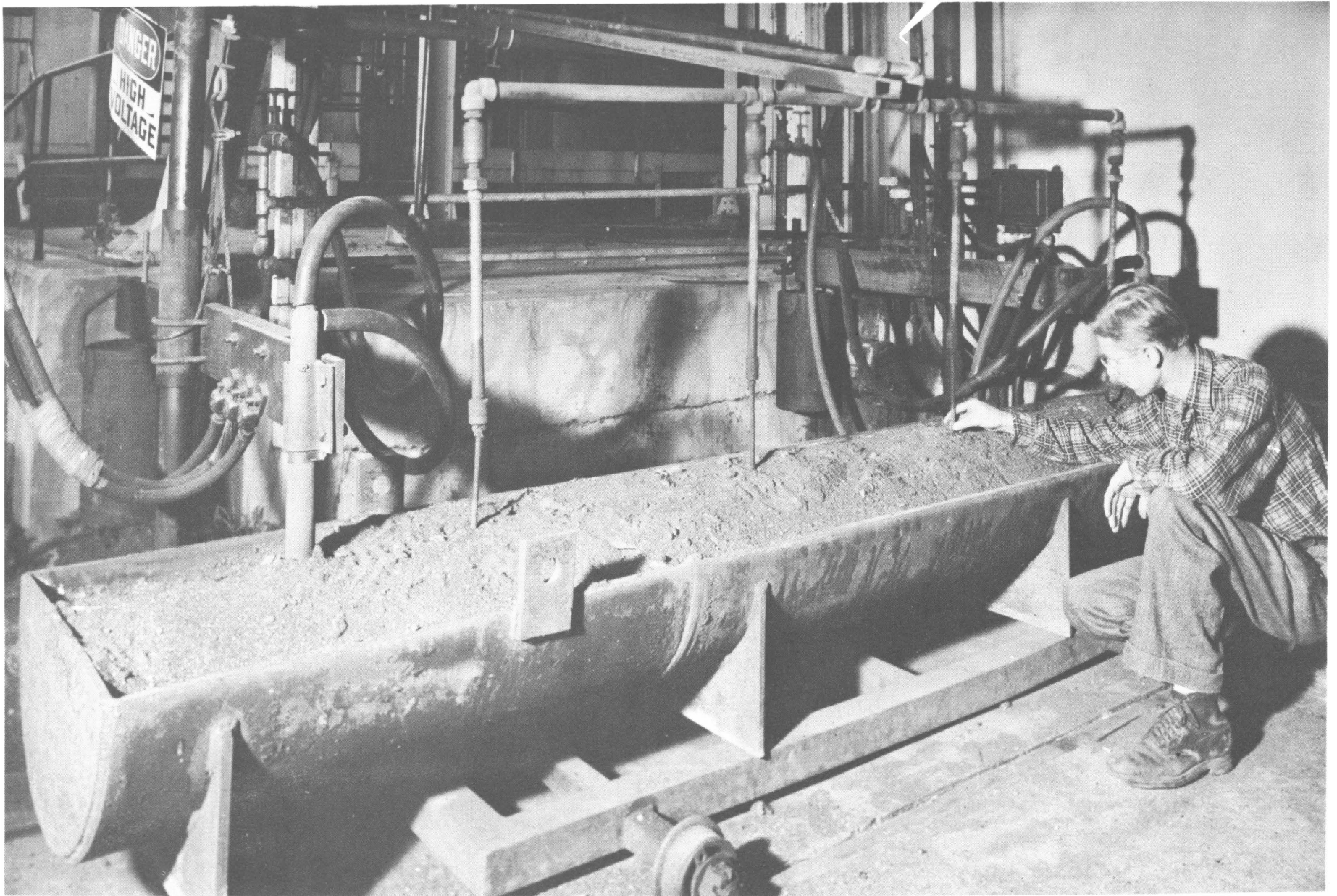


Figure 19 - Preparing to make Fischer-Tropsch synthesis catalyst by fusion method.

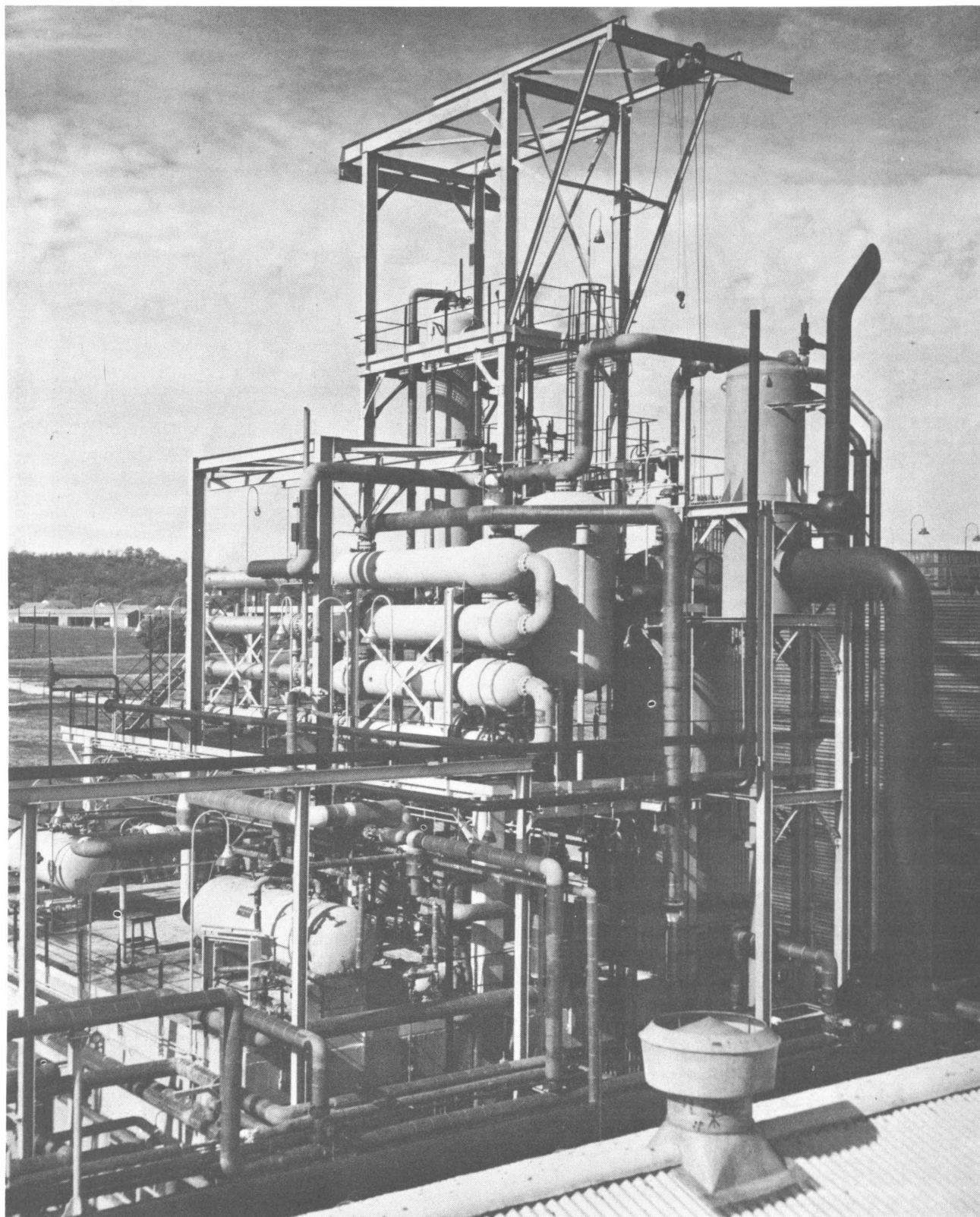


Figure 20. - Synthesis structure showing heat-exchange equipment (light vessels) and Fischer-Tropsch reactor (dark vessel at right center).

velocity limits, it became necessary to modify the synthesis reactor. This modification consisted of installation in the reactor of a steel liner backed up by a ceramic mass, reducing the reactor diameter from 6 feet to 3.

Choice of a ceramic material for backing up the steel liner required considerable study and experimentation before a material was found that was dense enough and one which would not disintegrate upon heating to reaction temperature. It was essential that this backing material be sulfur-free to protect the catalyst. It also was essential that the material be available in a puttylike form to provide a monolithic lining. The material finally employed was a sand-lime mixture that could be made up as a plastic putty and rammed in place between the steel liner and the outer shell of the reactor. This material was cured for several days to a hard, dense substance, using steam at 400° F.

Following installation and curing of the liner, it was impregnated with oil so that coolant oil would not be absorbed during the synthesis operation. In this impregnation treatment a coolant-oil fraction obtained from the distillation of East White Lake crude oil was employed. Heating to near reaction temperature completed the impregnation treatment.

With the modified reactor described above, it is possible to operate at the optimum oil velocities required to disperse the catalyst and at gas space velocities from 300 to approximately 1,000.

To test the synthesis reactor, auxiliary equipment, and instruments, a series of circulation tests was made in which water and coarse sand, and later water and unreduced catalyst, were employed in place of the coolant oil and reduced catalyst normally used in synthesis operations. Much was learned from these operations about the functioning and limitations of equipment, and the conditions for obtaining the jigging bed in other than a laboratory- or pilot-plant-size reactor.

The first difficulty experienced was that the coolant-oil-circulation pumps lost suction at periodic intervals. This difficulty was caused by a vortex formed in a liquid-gas separator which carried gas along with the liquid to the pump suction. This was corrected by placing a baffle in the separator in a suitable location, so that the vortex was broken. Another difficulty was that uniform distribution of gas within the jigging bed was not obtained. This caused the gas to flow upward through the reaction space in large bubbles, creating a projectilelike effect that carried the sand over into the strainers, pumps, and other equipment. First attempt at correction was to install a screen ahead of the oil-overflow pipe, which was intended to keep the sand from being carried out of the reactor by the oil stream. The location of the gas inlet was changed, and introduction of steel balls in the bottom of the reactor to insure better dispersion of gas in the form of small bubbles in the liquid medium appeared to assist. Finally, installation of a baffle in the top of the reactor, substituting for the screen, permitted improved operation. When these tests were completed, the catalyst-water slurry was removed and the reactor allowed to drain thoroughly.

In the distillation unit, many changes in the piping, equipment, and instrumentation were found necessary. These were corrected as they were found in the course of preliminary testing operations, and by the time the first synthesis run was made, all components of the distillation system were in operating condition.

A series of actual operating tests was made on the Dowtherm vaporizer, primary fractionation system, absorbers, debutanizer, stabilizer, rerun column, and the vacuum still. One phase of these tests included distillation of 18,500 gallons of a low-sulfur crude oil from the East White Lake field into gasoline, naphtha, coolant oil, and residue fractions (fig. 21). The distilled fractions came up to all expectations and indicated that the desired cuts could be obtained in later operations. This fractionation of the crude oil yielded 8,000 gallons of a coolant-oil fraction containing 0.06 percent sulfur. This coolant oil was employed in the first synthesis run.

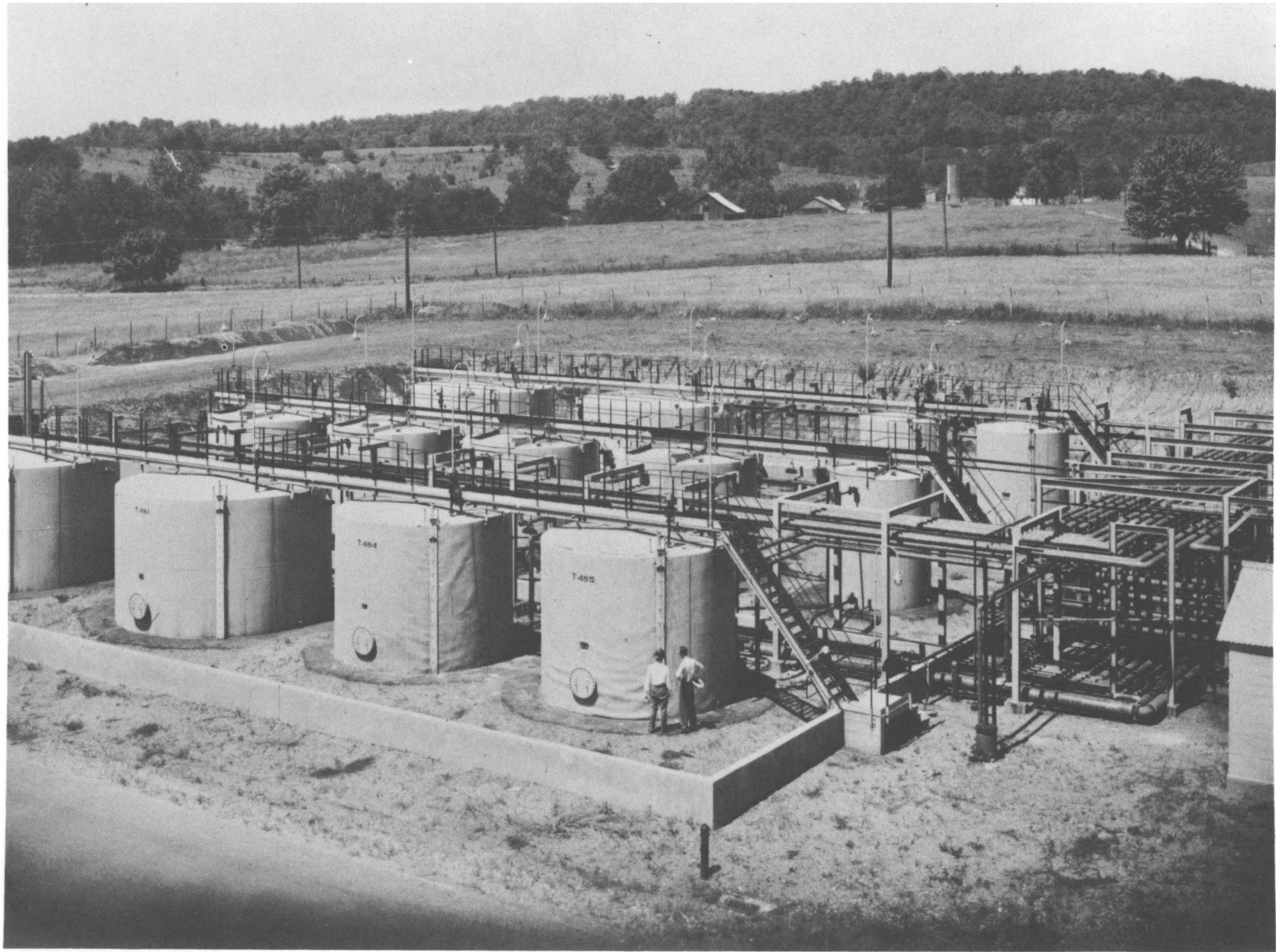
In these test runs, it was found that a new pump was required to transfer the primary column gasoline to the debutanizer, which operated at a pressure greater than the original pumps could generate. Various mechanical difficulties with the vacuum-distillation-system pumps and the gasoline pumps of the primary fractionator were corrected also. Outside of a few minor mechanical adjustments the Dowtherm, debutanizer, stabilizer, and rerun systems performed about as had been anticipated.

The final preparations for operation of the distillation unit included filling the converters of the Perco catalytic reforming unit with Cyclocel bauxite catalyst, and the converter of the U.O.P. catalytic polymerization unit with phosphoric acid catalyst. Following these operations, the entire distillation system was placed in standby condition ready for operation when the first synthesis run was made.

The carbon dioxide removal unit, which is used on the recycle-gas stream to the synthesis reactor and the feed-gas stream to the absorbers, required completion of its installation. The bubble-cap plates had to be installed in the reactivator, and the Raschig ring packing had to be placed in the carbon dioxide absorber. After the unit was placed in operating condition, it was subjected to various tests with water and inert gas to determine its operability. Finally, the water was drained from the system and replaced by a monoethanolamine solution, and the unit was ready for synthesis operations.

Synthesis Run 1

Synthesis run 1 had three objectives. The first was to operate the synthesis unit and obtain as great a conversion of gas into synthesis products as possible; second, to train further all operators and supervisors under actual operating conditions; and third, to observe the functioning of all equipment and instruments at operating temperatures and pressures. All three objectives were realized, and the run was considered satisfactory.



212686 O - 52 - 6 Figure 21. - Tankage area for intermediate and finished product storage in Gas-Synthesis Plant.

The run was begun on September 4 when heating of the coolant oil and circulation of gas and coolant oil through the synthesis reactor and auxiliaries were started. The initial oil rate was 250 g.p.m. and the fresh gas-feed rate was 60,000 standard cubic feet per hour. A recycle gas rate of 60,000 standard cubic feet per hour was maintained during the early stages of the run but was abandoned when coolant-oil losses through entrainment in the gas stream became excessive. The operating pressure was maintained at approximately 325 to 330 pounds per square inch gage (p.s.i.g.) throughout the run. Enough catalyst was employed in the synthesis reactor to permit a space velocity based on anticipated fresh feed gas of approximately 600 volumes per volume per hour.

During the induction period the temperature was gradually brought up to 450° F. and then further raised by 25° F. steps until evidence of reaction was obtained. The first indications of reaction (carbon dioxide in the gas stream leaving the reactor) were obtained at 500° F. However, it was necessary to raise the temperature to 550° F. when conversion in the range of 30 to 32 percent was obtained. The operating conditions existing during the latter part of the run were as follows:

Synthesis run 1

Average conditions for period of September 9-12, 1951

Maximum temperature, top of reactor	°F.	549
Temperature difference across reactor	do.	9
Maximum reactor pressure	p.s.i.g.	330
Pressure differential across reactor	do.	22
Fresh feed gas flow rate	std. cu. ft. hr.	56,300
Recycle ratio	No recycle	
H ₂ :CO ratio, fresh gas feed		0.82
H ₂ + CO conversion	percent	31
Usage ratio, H ₂ :CO		0.68
CO ₂ in fresh gas feed	percent	1.6
CO ₂ in gas stream leaving reactor	do.	11.8
CO ₂ in tail gas stream to absorber	do.	0.1
Synthesis products	gm./cu. m. H ₂ + CO feed (theo.)	64.5

The run was terminated on September 12 after 8 days of operation. It was evident that the catalyst activity was low, and this can be attributed to the following factors:

(1) The catalyst employed in this run was the first to pass through the reduction equipment and was not uniformly reduced. The percentage of reduction varied between zero and 100 percent and probably averaged about 70 percent.

(2) The catalyst was stored under coolant oil which contained 0.06 percent sulfur. Although the amount of sulfur was low, it could have had a deleterious effect on the catalyst.

(3) The circulating coolant oil in the system initially contained 0.06 percent sulfur, but this was reduced as the reaction progressed.

(4) The synthesis fresh feed gas contained excessive amounts of sulfur during the early stages of the synthesis.

Some of the difficulties experienced during this first synthesis run were corrected after the run was terminated, and the units were prepared for the second synthesis run which was made during October and November.

Synthesis Run 2

The synthesis and distillation units were operated in conjunction with the Kerpely gasifier and purification unit in a second synthesis run from October 23 to November 18, 1951. Included were the Fischer-Tropsch reactor system, the primary distillation column, the light-ends absorbers and stripper, the polymerization reactor, and the final stabilizer and rerun columns. Operation of the various units was relatively smooth, but some improvements in instrumentation and control could have added measurably to ease of operation.

Fourteen thousand pounds of reduced synthetic ammonia-type conversion catalyst, prepared and reduced in the plant, was charged to the synthesis converter on October 21 and 22, 1951. The catalyst was estimated to be approximately 90 percent reduced. This weight of catalyst had a volume of approximately 116 cubic feet, and permitted a space velocity of 550 volumes per volume per hour with a fresh synthesis gas feed rate of 65,000 standard cubic feet per hour. The reduced catalyst had been covered with a sulfur-free oil to prevent deterioration of the catalyst after reduction and during the storage period of approximately 6 months. Additional coolant oil, the fraction of East White Lake crude that had been used in the first synthesis run, was charged to the synthesis converter on October 23, 1951. After raising the pressure in the synthesis unit to 330 p.s.i.g., circulation and heating of the coolant oil to reaction temperature and the flow of synthesis gas to the converter were started. The initial oil circulation rate was 250 g.p.m., and the initial fresh synthesis-gas feed rate was approximately 62,000 standard cubic feet per hour. No recycle-gas flow was employed at the start.

A stepwise induction procedure was employed. This was similar to the procedure employed at the Bruceton laboratories but differed in the temperature and conversion levels used. This operation covered 5 days. The following shows the temperatures and conversions obtained during the catalyst induction period:

Catalyst induction

Date	Fresh feed rate, std. cu. ft. hr.	Recycle-feed rate	Temperatures, °F.		Conversion, percent
			In reactor	Out reactor	
10-23-51	61,600	None	294	294	-
10-24-51	63,200	1.13	428	431	13.5
10-25-51	61,500	1.27	451	457	21.5
10-26-51	63,100	1.27	474	485	35.6
10-27-51	64,700	1.27	505	522	62.0
10-28-51	63,900	1.36	509	524	71.6

Pressures were maintained within the range of 327 to 334 p.s.i.g. and oil circulation rates from 300 g.p.m. at the start to 500 g.p.m. during the latter phases of the induction period and during the synthesis period.

After the induction was completed, the temperatures during synthesis operations were maintained between 522° to 528° F., and conversions ranging from 71.6 to 85.9 percent were obtained. Conversion relates to the percentage of hydrogen and carbon monoxide consumed in the reaction, as determined by analysis of the inlet and outlet gas streams and volumes of each. No attempt was made to obtain maximum conversion, as the objectives of this run were to test the equipment and process for operability over an extended time.

Table 10 shows actual operating data obtained during a 5-day period of the run. The results are not intended to represent the optimum conditions or yields, which are to be determined in future runs.

These operations were conducted on a continuous basis from the start until the run terminated at the end of 25 days, with one exception. A forced shut-down, occurring on November 11 and lasting for 30 hours, owing to an interruption of the 275-p.s.i.g. steam supply to the entire synthesis area, was successfully bridged and gave the operators valuable experience in handling an unexpected situation. Although some drop in catalyst activity resulted from this interruption, 75-percent conversions were still obtained at 525° F. at the termination of the run. The final shut-down was routine.

Distillation of the synthesis condensate into gasoline, Diesel oil, cracking-stock, and coolant-oil fractions was accomplished during the latter part of November. The principal products, gasoline and Diesel oil, will be upgraded by further treatments and will be available in barrel quantities for evaluation and testing.

TABLE 10. - Average operating conditions, synthesis run 2

Date	11-2-51	11-3-51	11-4-51	11-5-51	11-6-51
Fresh feed gas flow std. cu. ft. hr.	62,700	62,200	62,600	63,200	61,900
H ₂ :CO fresh feed gas	0.76	0.80	0.80	0.79	0.76
Recycle ratio	1.45	1.58	1.55	1.53	1.63
Maximum temperature °F.	523	522	523	522	524
dT across converter do.	15	14	15	14	15
Maximum pressure p.s.i.g.	327	330	329	330	329
dP across converter p.s.i.	30	30	31	31	30
Space velocity vol./vol./hr.	538	534	537	542	531
Conversion percent	81.9	81.7	80.6	79.8	85.9
Usage ratio	0.70	0.71	0.70	0.71	0.71
CO ₂ :					
In fresh feed gas percent	1.5	2.2	1.6	2.5	2.0
In recycle gas do.	1.9	0.0	0.1	0.4	0.1
In gas from synthesis converter do.	12.5	11.8	11.5	11.4	12.2
C ₁ + C ₂ yield gm./m ³ (CO + H ₂) in fresh feed	35.7	35.6	34.2	29.0	24.6
C ₃ + yield gm./m ³ (CO + H ₂) in fresh feed (theo.)	134.6	135.3	133.5	137.0	154.0

Engineering and Economic Studies for Commercial-Size Operations

Rock Springs, Wyo., and Western Kentucky (30,000-Barrel-per-Day Coal Hydrogenation Plant)

Three studies were completed during the year dealing with the economics of commercial-size coal-hydrogenation plants. One consisted mainly of a review of Bureau of Mines Report of Investigations 4564, Estimated Plant and Operating Cost for Producing Gasoline by Coal Hydrogenation, which was prepared in 1948 and issued in August 1949. The purpose of the review was to present an up-to-date cost estimate and to determine the average return on equity capital after allowing for all normal operating and capital charges and taxes, assuming that 50 percent of all capital requirements is funded debt and 50 percent equity capital. Whereas the previous report was concerned only with the cost of making synthetic fuels, this new report considers the current selling price of the products and uses a realistic capital structure comparable with recent industry trends. The process used was the so-called "conventional plant" as described in Report of Investigations 4564, with certain minor improvements that are well enough developed at present to assure successful operation.

The improvements are as follows:

- (1) The liquid-phase hydrogenation was adjusted to reflect the use of wrapped-vessel construction instead of the forged vessels originally used.
- (2) The liquid-phase and vapor-phase hydrogenation was adjusted to reflect an increase in throughput of 10 percent because instrumentation was more complete than in the German plants.
- (3) Drum coking was substituted for the flash-distillation unit.
- (4) The product distribution shown in the new report differs from that shown in Report of Investigations 4564. Since the latter report was issued, the coals reported on in the new report have been processed at the demonstration plant, and the new product distribution is based on the results obtained.
- (5) An aromatic separation unit was added to recover the benzene, toluene, and xylene present in the vapor-phase gasoline. The decision to include this unit was based on the fact that the chemicals that could be produced in a coal-hydrogenation plant are in high demand. Today's increased demand for benzene and avgas plus a growing market for tar acids has justified the inclusion of chemical production in the synthetic fuel picture.

As a result of this first study, two cost estimates were prepared - one for a single 30,000-barrel-per-calendar-day plant in Wyoming, and the second for a similar plant in Western Kentucky. Table 11 shows the plant-cost summaries for the two operations. Several sections of these estimates have been reviewed by Ebasco Services, Inc.; the estimates shown herein represent the Bureau of Mines data adjusted to conform to the results of this review wherever applicable. The points covered by Ebasco were the power plant, hydrogen purification and compression, company-financed housing and community facilities, operating costs, financing program, and a market survey of the aromatic and tar acid products.

TABLE 11. - Cost summary for coal-hydrogenation plant of conventional design

	Rock Springs 30,000 bbl. per calendar day	Western Kentucky 30,000 bbl. per calendar day
Coal-preparation plant	\$ 6,680,000	\$ 6,680,000
Paste-preparation plant	3,180,000	3,160,000
Liquid-phase hydro plant	54,000,000	58,700,000
Delayed-coking plant	7,550,000	8,710,000
Vapor-phase hydro plant	30,250,000	30,250,000
Product-distillation unit	11,700,000	11,250,000
Tar-acid-recovery unit	2,510,000	2,510,000
Low-temperature separation unit	7,510,000	8,000,000
Hydrocarbon-steam-cracking unit	9,150,000	9,810,000
Coal-gasification unit	5,970,000	4,860,000
Oxygen plant	8,800,000	7,320,000
H ₂ -purification and compression	56,184,000	53,664,000
Tankage	7,060,000	7,060,000
Power plant	51,400,000	51,400,000
Plant utilities	37,000,000	37,000,000
General plant facilities	27,975,000	28,000,000
Aromatic-extraction unit	5,000,000	4,700,000
Water supply	18,000,000	2,000,000
Total plant cost	349,919,000	335,074,000
(tax and insurance base)		
Interest during construction	15,657,000	15,112,000
Subtotal	365,576,000	350,186,000
(for depreciation)		
Paid-up royalties	2,000,000	2,000,000
Housing assistance fund	250,000	250,000
Cost of mine development	13,000,000	19,430,000
Total fixed investment	380,826,000	371,866,000
Working capital	20,000,000	20,000,000
Total investment	\$400,826,000	\$391,866,000

The over-all capital investment for a 30,000-barrel-per-calendar-day coal-hydrogenation plant, processing Wyoming bituminous coal, is \$400,826,000, including the coal mine, power plant, working capital, and employee housing assistance. Calculations show that the average return, based on present market prices of product (see table 12), on \$200,413,000 equity capital would be 2.81 percent after taxes and may be increased to 3.59 percent on \$201,913,000 equity capital by the addition of sulfur- and ammonia-recovery equipment which adds \$3,000,000 to the total capital requirements. On the same basis the capital investment for a plant processing Western Kentucky coal is \$391,866,000, and the average return on \$195,933,000 equity capital is 5.21 percent after taxes. Sulfur- and ammonia sulfate-recovery facilities would increase the total capital requirements to \$395,986,000 and the average return after taxes would be 6.22 percent on \$197,933,000.

Tables 11A and 11B show detailed operating cost summaries for the two plants.

The coal price used includes all mining costs, as well as depreciation, welfare payments, royalties, etc., but excludes profit on the mine investment and sales expense.

Operating and maintenance labor requirements are based on a detailed organization chart and amount to 260 operating men per shift, and 1,170 maintenance workers.

Payroll overhead amounts to about 18 percent of the labor payroll and includes vacations, social security, sick leave, workmen's compensation, and other benefit programs.

The administrative and indirect operating costs are based on a detailed analysis of the entire plant.

Fixed costs include 1 percent of plant investment to cover local, county, and State taxes, and plant insurance. Depreciation is included at 4 percent, which corresponds to an average plant life of 25 years.

Figure 22 is the flow diagram and material balance for the Western Kentucky base plant. The motor fuel produced exceeds present specifications for regular-grade gasoline and has a research octane number of 83 clear before separation of aromatics. It is estimated that 1 cc. of tetraethyllead will be required to give premium-grade gasoline after aromatics separation. In addition to gasoline and LP-gas, basic chemicals, which are in heavy demand and command a high selling price, as compared to fuels, are produced by coal hydrogenation. The two groups of chemicals that coal hydrogenation produces most readily are (1) aromatic hydrocarbons, such as benzene, toluene, and xylene, and (2) tar acids, such as phenol, cresols, and xylenols. The product stream is rich in these chemicals, and they can be extracted and recovered without difficulty.

TABLE 11A. - Rock Springs, Wyo. - 30,000-barrel-per-calendar-day plant
of conventional design

Operating costs and financial analysis

a. Raw materials:	
Coal, 14,800 tons per stream day x 330 x \$2.50	\$12,200,000
Catalyst, chemicals, \$5,429 per day	1,790,000
Tetraethyllead	828,000
b. Direct labor:	
Operating labor, 260 per shift	4,713,000
Operating supervision	645,000
c. Plant maintenance, 1,170 men	4,974,000
Material	5,873,000
d. Payroll overhead	1,890,000
e. Operating supplies	712,000
Total direct cost	<u>33,625,000</u>

Indirect cost

General administrative	1,978,000
Indirect operating cost	<u>2,048,000</u>
Total indirect cost	<u>4,026,000</u>

Fixed costs

Local, county, and State taxes, insurance at 1 percent	3,499,000
Depreciation at 4 percent	<u>14,623,000</u>
	18,122,000
Cost of operation without profit and interest	55,773,000
Cost per gallon of total product (460,000,000 gal.)	12.1¢

Financial analysis^{1/}

	<u>With ammonia and sulfur recovery</u>	<u>Without ammonia and sulfur recovery</u>
Total value of products	\$76,181,000	\$69,927,000
Cost of operation without profit and interest	<u>58,753,000</u>	<u>55,773,000</u>
Gross profit	17,428,000	14,154,000
Interest on funded debt(3-1/2 percent) ^{2/}	<u>3,675,000</u>	<u>3,650,000</u>
	13,753,000	10,504,000
Coal depletion allowance at \$0.15 per ton	<u>732,000</u>	<u>732,000</u>
Taxable net income :	13,021,000	9,772,000
Income taxes at 50 percent	<u>6,511,000</u>	<u>4,886,000</u>
Net income after taxes	6,510,000	4,886,000
Coal depletion allowance	<u>732,000</u>	<u>732,000</u>
Net funds available	7,242,000	5,618,000
Net funds as percent of (unchanged) equity capital ^{3/}	3.59	2.81

^{1/} Average year of operation.

^{2/} 50 percent of total investment.

^{3/} 50 percent of total investment.

TABLE 11B. - Western Kentucky, Union County - 30,000-barrel-per-calendar-day
plant of conventional design

Operating costs and financial analysis

a. Raw materials:	
Coal, 14,720 tons per stream day x 330 x \$2.50	\$12,120,000
Catalyst and chemicals, \$5,400 per day	1,780,000
Tetraethyllead	775,000
b. Direct labor:	
Operating labor, 260 per shift	4,713,000
Operating supervision	639,000
c. Plant maintenance, 1,170 men	4,968,000
Material	5,873,000
d. Payroll overhead	1,878,000
e. Operating supplies	697,000
Total direct cost	33,433,000

Indirect cost

General administrative	1,895,000
Indirect operating costs	2,027,000
Total indirect cost	3,922,000

Fixed costs

Local, county, and State taxes, insurance at 1 percent	3,351,000
Depreciation at 4 percent	14,007,000
	17,358,000
Cost of operation without profit and interest	54,723,000
Cost per gallon of total product (460,000,000 gal.)	11.9¢

Financial analysis^{1/}

	<u>With ammonia and sulfur recovery</u>	<u>Without ammonia and sulfur recovery</u>
Total value of products	\$86,658,000	\$79,173,000
Cost of operation without profit and interest	57,715,000	54,723,000
Gross profit	28,943,000	24,450,000
Interest on funded debt(3-1/2 percent) ^{2/}	3,604,000	3,565,000
	25,339,000	20,885,000
Coal depletion allowance at \$0.15 per ton	730,000	730,000
Taxable net income	24,609,000	20,155,000
Income taxes at 53 percent	13,030,000	10,680,000
Net income after taxes	11,579,000	9,475,000
Coal depletion allowance	730,000	730,000
Net funds available	12,309,000	10,205,000
Net funds as percent of (unchanged) equity capital ^{3/}	6.22	5.21

^{1/} Average year of operation.

^{2/} 50 percent of total investment.

^{3/} 50 percent of total investment.

A market survey was made to determine the quantity of products that could be absorbed without reduction in price. The amount of chemicals credited to the operation in each case was determined on the basis of this survey. For each of the plants all potential chemical byproducts, except o-cresol, m-p-cresol and the xlenols, are believed to be marketable at current prices. The maximum production of these materials was limited as follows: 6,800,000 pounds of o-cresol, 50,000,000 pounds of m-p-cresol and 25,000,000 of xlenol.

Table 12 shows the quantity and products produced in both Rock Springs, Wyo., and the Western Kentucky 30,000-barrel-per-calendar-day cases.

Southern Colorado (15,000-Barrel-per-Day Coal-Hydrogenation Plant)

In the two remaining economic studies completed during the year, specific sites were chosen that could be considered for synthetic fuel production. It should be noted that the plants considered in these economic studies include numerous improvements over the so-called conventional plants discussed previously. Also, platforming units are included for maximum chemicals production. These estimates, therefore, are not directly comparable to the Rock Springs, Wyo., and the Western Kentucky studies presented above.

For the first of these studies a location in southern Colorado was selected. The site had the following factors that appeared to be very attractive: (1) Ample coal supply, (2) available labor market, (3) railroad adjacent to plant site, (4) natural gas available at 15 cents per 1,000 cubic feet and (5) purchased power available in amounts up to 50,000 kilowatts at 5-1/2 mills.

Table 13 is a preliminary plant-cost summary of a 15,000-barrel-per-calendar-day coal-hydrogenation plant at the Colorado site using natural gas for hydrogen production and purchasing 50,000 kw.-hr. of electrical energy.

Figure 23 is a flow diagram and material balance showing throughput quantities and products.

Northern Wyoming (15,000-Barrel-per-Day Coal-Hydrogenation Plant)

The other economic study was for a 15,000-barrel-per-day coal-hydrogenation plant in northern Wyoming. The site chosen had the following advantages: (1) Ample supply of very cheap coal, (2) water supply ample for once-through cooling, (3) United States highway passing by plant site, and (4) natural gas possibly available.

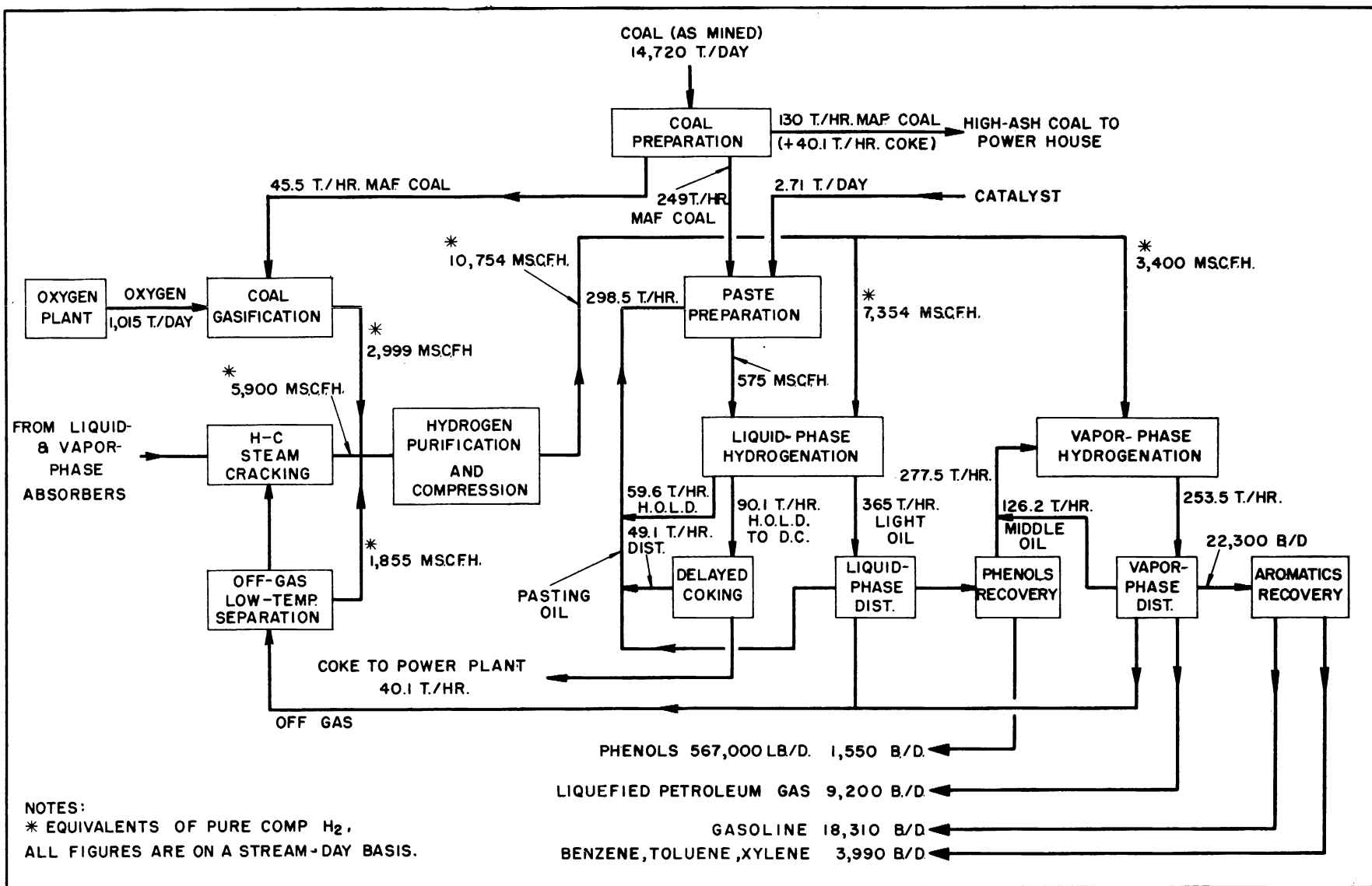


Figure 22. - Flow diagram of coal-hydrogenation plant to produce 30,000 barrels per calendar day (33,050 barrels per stream day) from Western Kentucky Union County coal.

TABLE 12. - Product quantity and value ... Rock Springs, Wyo. - 30,000-barrel-
per-calendar-day plant of conventional design

	Products		Annual value
Benzene gal. per yr.	11,750,000	at \$0.335 gal.	\$ 3,936,250
Toluene-xylene do.	39,350,000	at .285 gal.	11,214,750
Phenol lb. per yr.	43,800,000	at .155 lb.	6,789,000
m-p-Cresol do.	50,000,000	at .155 lb.	7,750,000
o-Cresol do.	6,600,000	at .155 lb.	1,023,000
Xylenol do.	25,000,000	at .135 lb.	3,375,000
Ammonium sulfate tons per yr.	131,000	at 45.00 ton	5,895,000
Sulfur do.	17,100	at 21.00 ton	359,100
Motor fuel gal. per yr.	286,260,000	at .11 gal.	31,488,600
LP-gas do.	108,800,000	at .04 gal.	4,350,000
			<u>76,180,700</u>

Aromatic hydrocarbons reduced by 3.5 cents per gallon for freight differential.
Tar acids reduced by 1.5 cents per pound for freight differential.

Product quantity and value ... Western Kentucky, Union County - 30,000-barrel-
per-calendar-day plant of conventional design

	Products		Annual value
Benzene gal. per yr.	12,700,000	at \$0.37 gal.	\$ 4,700,000
Toluene-xylene do.	42,390,000	at .32 gal.	13,565,000
Phenol lb. per yr.	77,000,000	at .17 lb.	13,090,000
m-p-Cresol do.	50,000,000	at .17 lb.	8,500,000
o-Cresol do.	6,800,000	at .17 lb.	1,155,000
Xylenol do.	25,000,000	at .15 lb.	3,750,000
Ammonium sulfate tons per yr.	129,000	at 45.00 ton	5,805,000
Sulfur do.	80,000	at 21.00 ton	1,680,000
Motor fuel gal. per yr.	255,210,000	at .11 gal.	28,073,000
LP-gas do.	126,800,000	at .05 gal.	6,340,000
			<u>86,658,000</u>

TABLE 13. - Cost summary for 15,000-bbl.-per-calendar-day coal hydrogenation plant in southern Colorado

Coal-cleaning plant	\$ 1,680,000
Paste-preparation unit	2,170,000
Liquid-phase hydrogenation unit	37,000,000
Liquid-phase distillation unit	1,490,000
Phenol-recovery unit	1,500,000
Vapor-phase hydrogenation unit	16,500,000
Refining section	9,355,000
Continuous-coking unit	2,240,000
Water gas sets	1,000,000
H-C-combustor unit	1,960,000
Oxygen plant	7,900,000
Oxygen-compression unit	1,080,000
H ₂ -purification and compression unit	13,000,000
Tankage	3,450,000
Utilities	12,500,000
Power plant (50,000 kw. purchased)	15,000,000
General plant facilities	12,500,000
Total construction	140,325,000
Contingency (additional 10 percent)	14,000,000
Total plant cost (tax and insurance base)	154,325,000
Interest during construction	7,140,000
Paid-up royalties	2,500,000
Subtotal (for depreciation)	163,965,000
Cost of mine development	6,060,000
Total fixed investment	170,025,000
Working capital	12,000,000
Total investment	\$ 182,025,000

As the natural-gas supply required for the production of hydrogen was questionable, two plans were undertaken. One depended on a supply of natural gas and the other on operating with a minimum of extraneous gas. This latter arrangement involved the direct-pressure gasification of H.O.L.D. as a source of hydrogen. This required a slightly greater throughput in the liquid-phase hydrogenation and a 26-percent increase in total hydrogen requirements but would eliminate the need for coking operations on the H.O.L.D., and the overall economics are not penalized. A larger initial investment is required, however, as shown in table 14, which outlines the comparative costs for the alternate designs. Both designs are based on liquid-phase hydrogenation at only 6,000 p.s.i.g. pressure, owing to the greater reactivity of the low-rank coal available.

Figures 24 and 25 show the respective flow quantities and products for the two designs.

TABLE 14. - Cost summary for 15,000-bbl.-per-calendar-day coal-hydrogenation plant in northern Wyoming

Unit	H ₂ from natural gas	H ₂ from H.O.L.D. gasification
Coal-cleaning plant	\$ 3,740,000	\$ 4,420,000
Coal-preparation plant	2,000,000	2,860,000
Paste preparation	2,100,000	2,620,000
Liquid-phase hydrogenation	19,050,000	22,760,000
Liquid-phase distillation	1,640,000	2,030,000
Phenol recovery	1,500,000	1,500,000
Vapor-phase hydrogenation	9,640,000	9,640,000
Refining	9,320,000	9,400,000
Continuous coking unit	2,720,000	-
Water gas sets	1,450,000	-
H.O.L.D. combustor	-	2,090,000
H-C combustor	1,985,000	635,000
Oxygen compressor	855,000	1,485,000
H ₂ purification and compression	14,520,000	17,100,000
Tankage	3,450,000	3,450,000
Oxygen plant	7,900,000	12,600,000
Utilities	9,800,000	11,000,000
Power plant	26,000,000	29,250,000
General plant facilities	10,000,000	10,000,000
Total construction	127,670,000	142,840,000
Contingency (additional 5 percent)	6,380,000	7,140,000
Total plant cost (tax and insurance base)	134,050,000	149,980,000
Interest during construction	6,220,000	6,970,000
Paid-up royalties	2,500,000	2,500,000
Subtotal (for depreciation)	142,770,000	159,450,000
Land, water, and coal	5,000,000	5,000,000
Total fixed investment	147,770,000	164,450,000
Working capital	11,500,000	12,000,000
Total capital requirements	159,270,000	176,450,000

The two economic studies of proposed 15,000-barrel-per-calendar-day coal-hydrogenation plants included process improvements and equipment arrangements representing the latest thoughts on commercial coal-hydrogenation designs. The improvements, though differing from the so-called "conventional plant," are not particularly revolutionary. Many of the improvements have gone beyond the pilot-plant stage and could be developed to commercial status readily within 12 months.

Work on the cost estimate for a 10,000-barrel-per-day coal-gasification and gas-synthesis plant continued. Recommended process alterations are being studied and considerable work remains to be done.

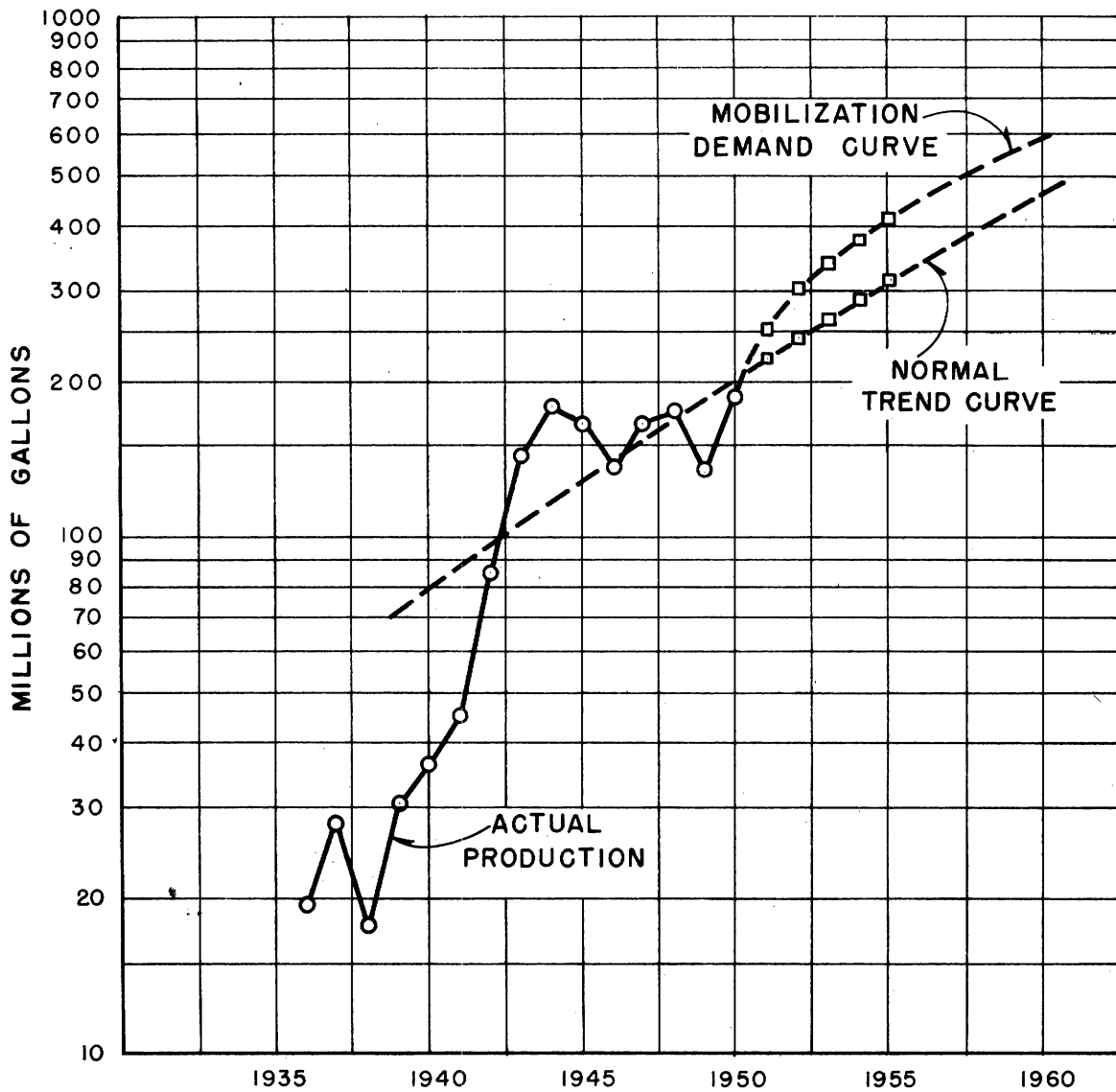
Aromatic Hydrocarbons and Chemicals from Synthetic Liquid-Fuel Plants

The continuing shortages in the supply of aromatic hydrocarbons, particularly benzene, and the tar acids became more acute during 1951. The conventional sources are completely inadequate to meet the enormously increased demand, and the shortages must be supplied by imports from foreign countries, from petroleum refining, and, eventually, from commercial coal-hydrogenation plants.

As more information on the composition of the coal-hydrogenation products made in the demonstration plant was obtained, it has been possible to revise earlier estimates and determine the position of coal-hydrogenation plants in supplying part of the shortage of the aromatic hydrocarbons and chemicals. The most recent analytical data support and extend all claims and estimates previously made.

To estimate the demand for aromatic hydrocarbons and chemicals in 1951-60, a series of production and market studies was made. In these studies, all pertinent statistical information relating to the production and distribution of benzene, toluene, xylene, phenol, the cresols, and cresylic acid (xylenols) was carefully analyzed, and trend lines were established for each commodity covering a span of years before 1951. By extending these trend lines to 1960, an estimate of the possible production required to meet the normal peacetime and mobilization demands was obtained. An example of this work is figure 26, showing the actual production and projected demand for chemical-grade benzene over the period 1936-60.

Except for m-p-cresol and the xylenols, the studies indicate that all the chemicals from a 30,000-barrel-per-day coal hydrogenation plant could be readily marketed. While most of the cresols could be marketed and a substantial amount of the xylenols could be absorbed, the excess production of these materials would have to be recycled to the plant and converted into fuels, pending the development of expanded markets for these chemicals.



○ DENOTES TARIFF COMMISSION DATA.

□ DENOTES INDUSTRY TASK-COMMITTEE ESTIMATE.

Figure 26. - Actual production and projected demand of chemical-grade benzene, 1936-60.

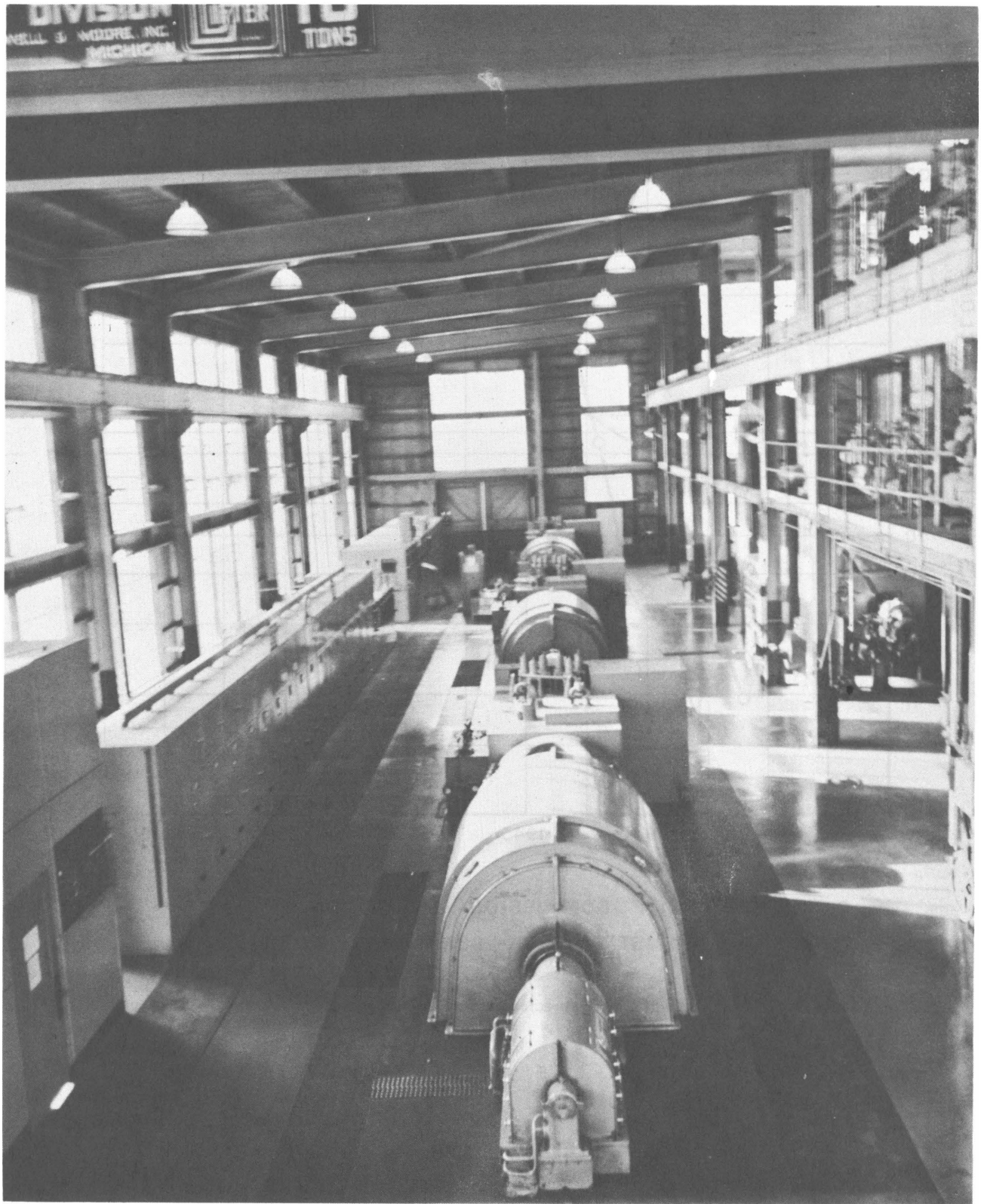


Figure 27. - Main operating floor in powerhouse, showing control boards and turbine generators.

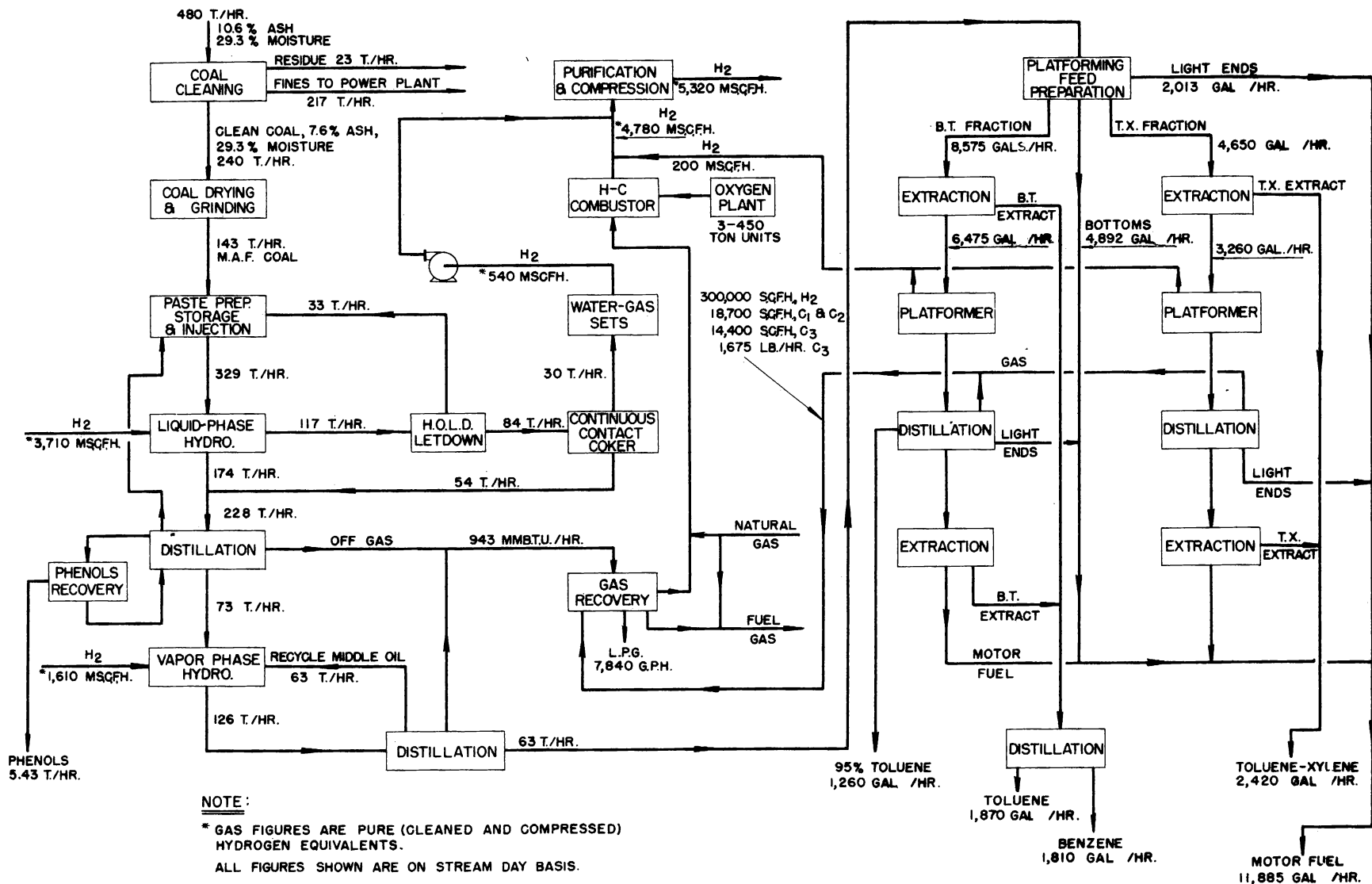


Figure 24. - Flow diagram of Northern Wyoming 15,000-barrel-per-calendar-day coal-hydrogenation plant; hydrogen produced from natural gas.

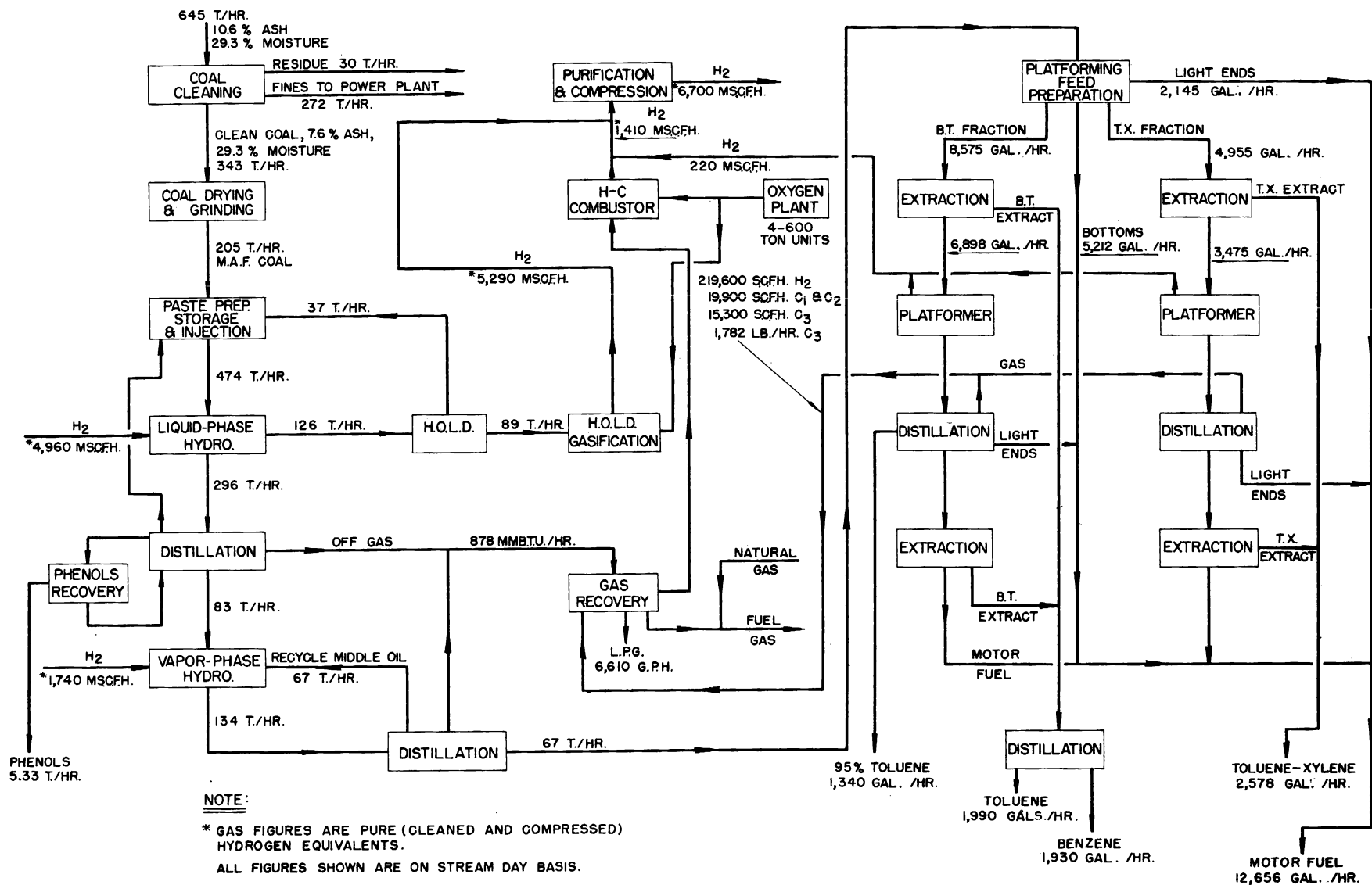


Figure 25. - Flow diagram of Northern Wyoming 15,000-barrel-per-calendar-day coal-hydrogenation plant; hydrogen produced by gasification of H.O.L.D.

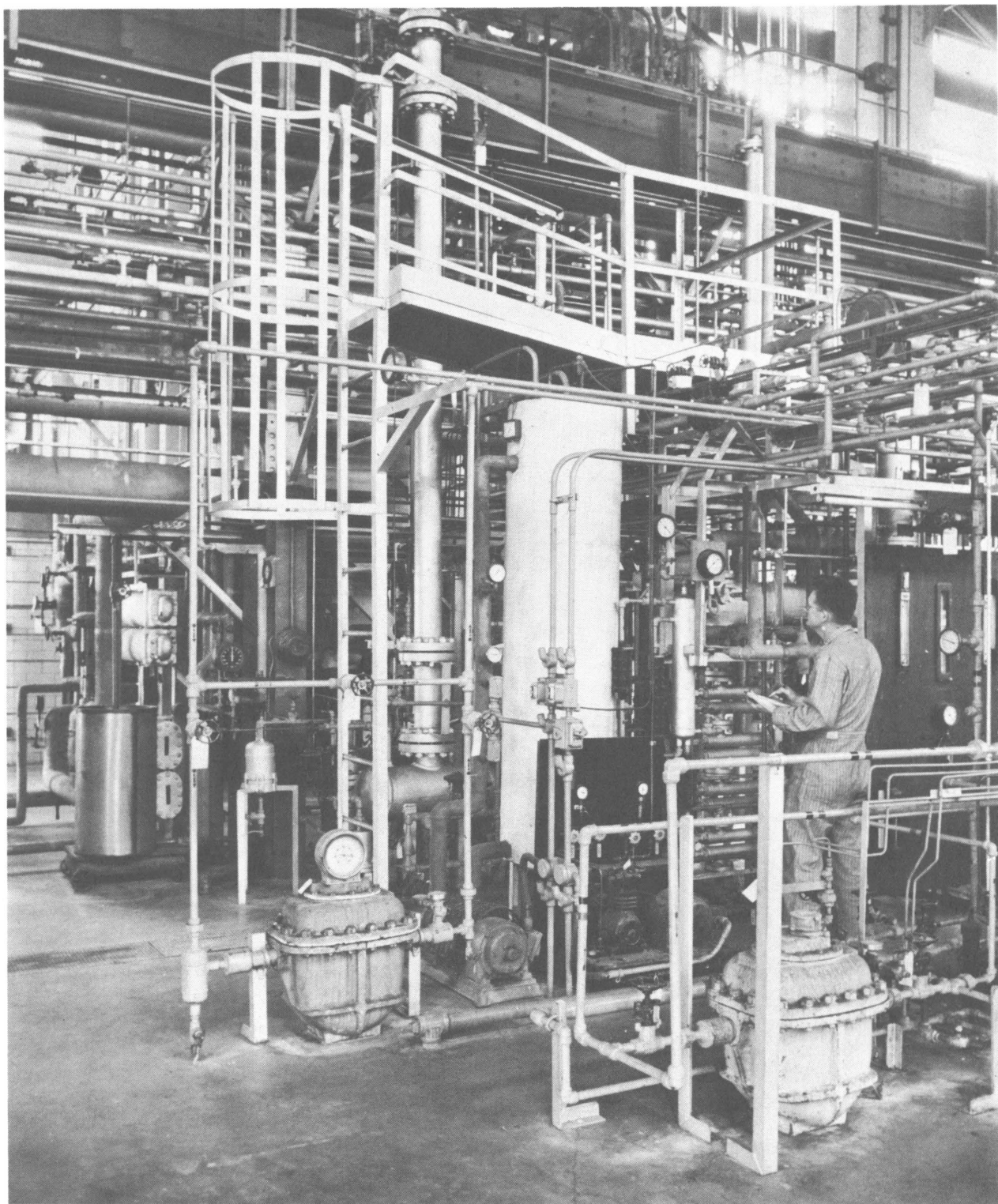


Figure 28. - Barrel-per-day Fischer-Tropsch plant.

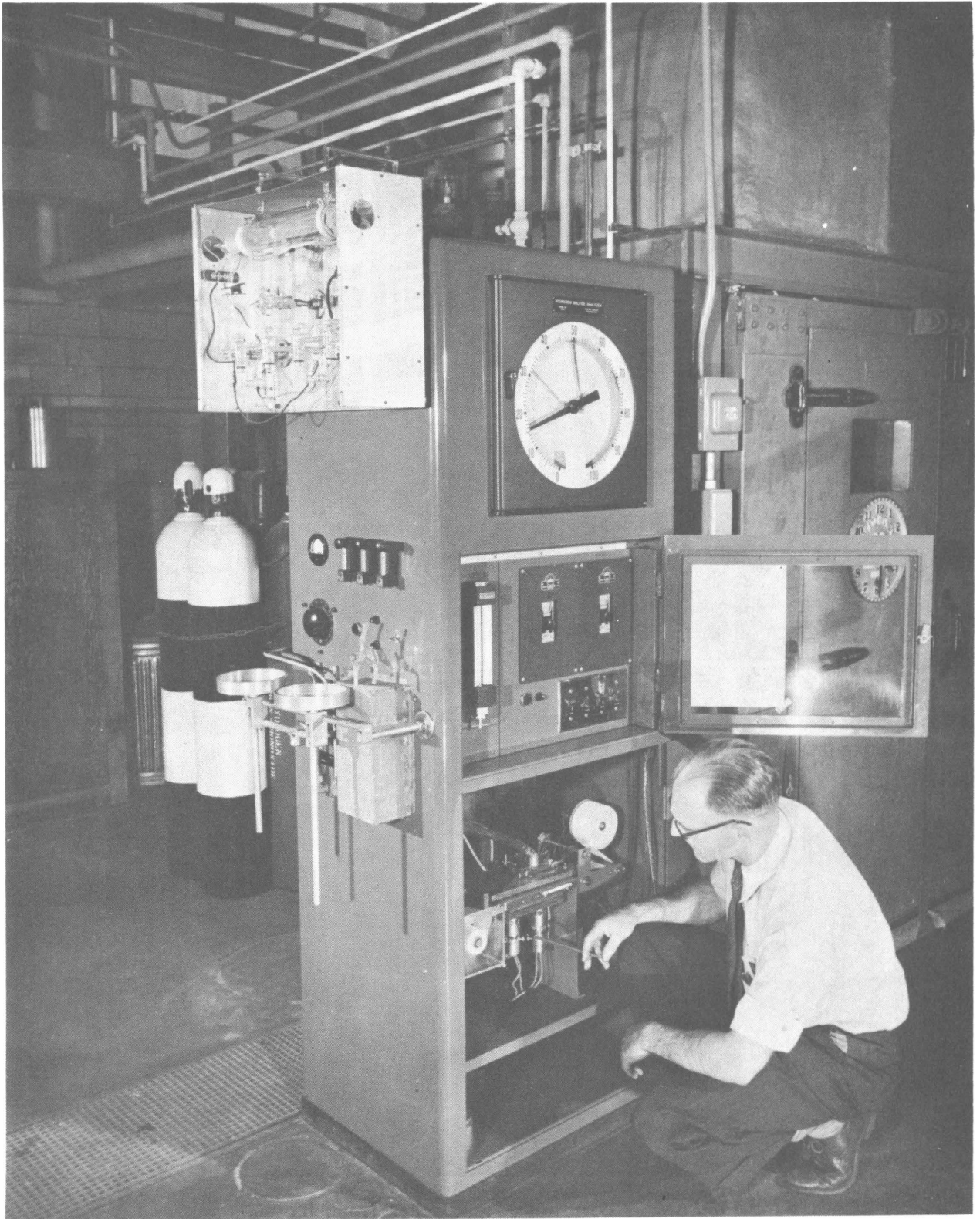


Figure 29. - Hydrogen sulfide analyzer.

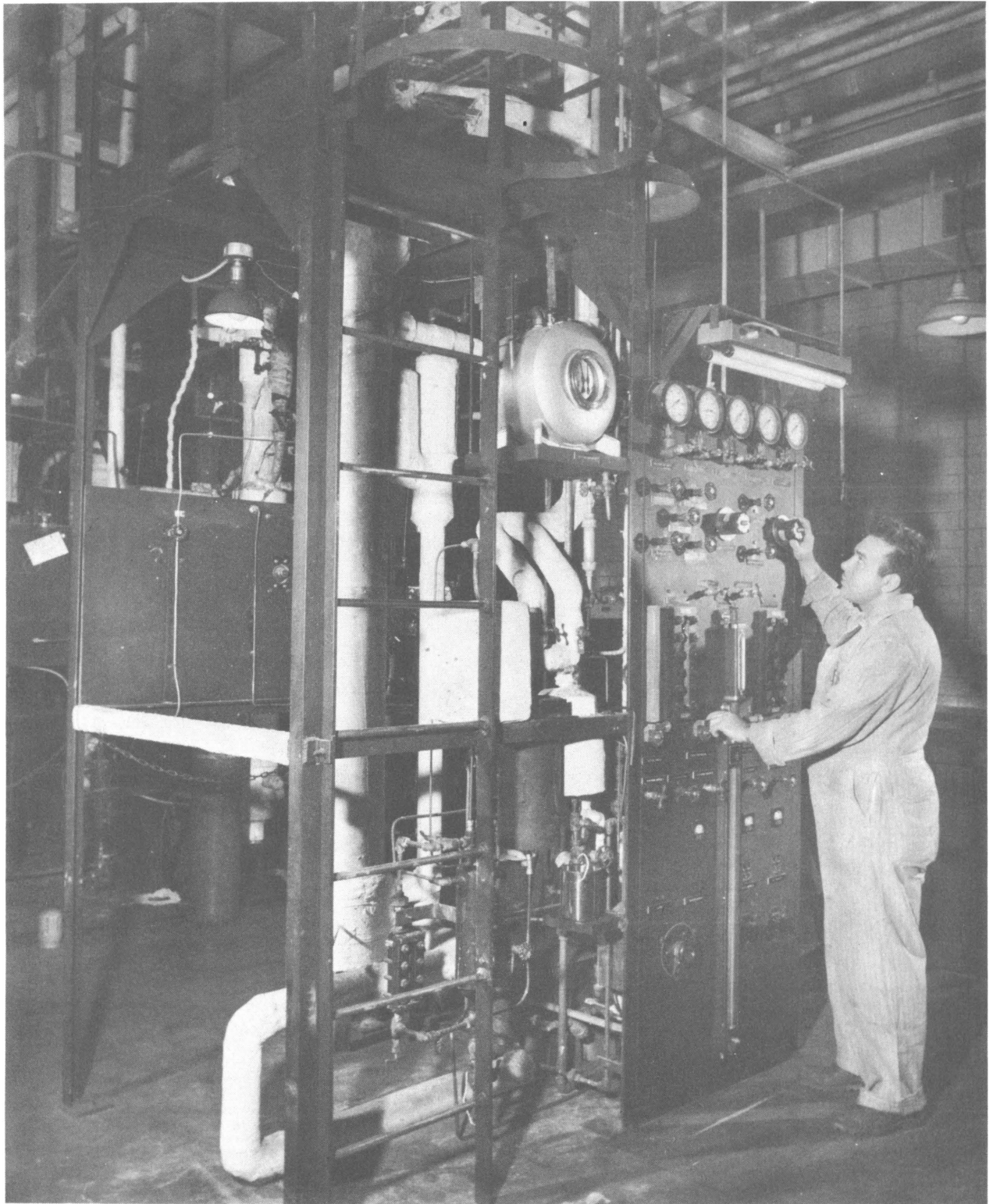


Figure 30. - Unit for fluidized Fischer-Tropsch process.

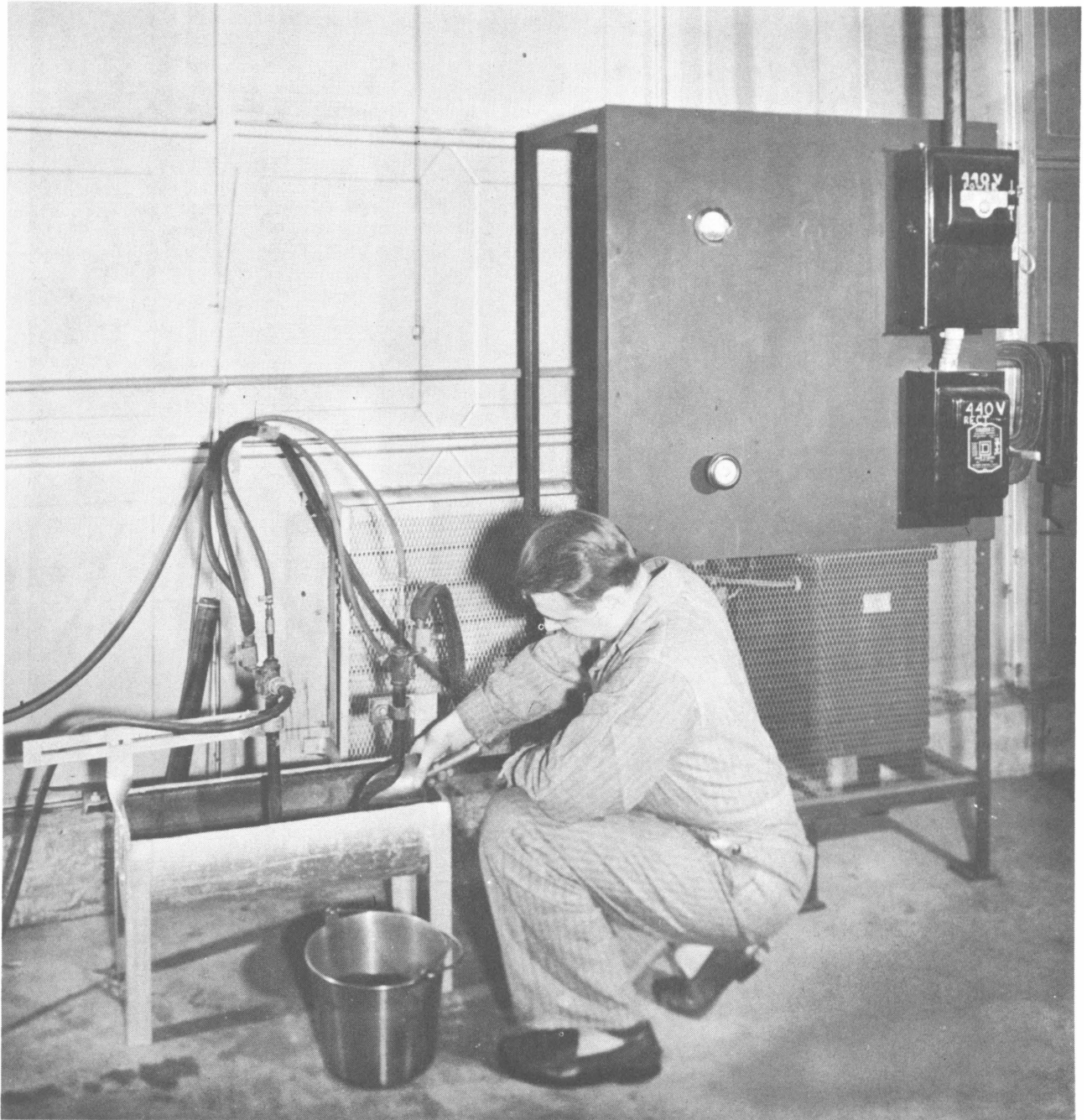


Figure 31. - Small fusion unit.

General

Power-Plant Operation

The power plant (see fig. 27) continues to provide all the electric power and steam for process work, prime movers, and all heating purposes, plus plant water and compressed air for the entire installation. Since January 1, 1950, operation of the hydrogenation, synthesis, and gas-manufacturing plants, with the added load of power sale to outside consumers, has advanced the average demand to 8,000 kw.-hr. for 1951, with a peak in excess of 13,000 kilowatts. Approximately 100,000 pounds per hour of process steam is necessary to operate the synthetic fuels plants. This, with the steam for electric power production, has established a peak of over 300,000 pounds per hour and fully loaded two of the three boilers installed at the power plant.

It is estimated that, in the 1951-52 fiscal year, the plant will generate some 66,000,000 kw.-hr. of electricity. Approximately 30,000,000 will be used for synthetic fuels and the surplus or excess power furnished to outside customers. Since 1948, the production cost of electric current has decreased from an average of approximately 5 cents to a present cost of 8 mills per kilowatt-hour. A considerable amount of maintenance has been done in the power plant. In the past 18 months two turbines have been rebladed, and a complete new power-cable system, sectionalizing switches, and high-speed relays have been installed with a decided reduction in operating expense.

Safety

Much attention has been given to the prevention and control of skin irritations.

All portions of the plant have operated throughout the year with a "zero" frequency and severity rate for disabling injuries. This unusual safety record in a plant subject to the inherent hazards of synthetic fuel processes is very gratifying and can be attributed at least in part to the sincere concern of everyone in accident and fire prevention.

RESEARCH AND DEVELOPMENT, COAL-TO-OIL LABORATORIES AND PILOT PLANTS,
BRUCETON AND PITTSBURGH, PA.

Research at the Bruceton, Pa., laboratories and pilot plants on the synthesis of liquid fuel from gasified coal (Fischer-Tropsch and related processes), on the production of liquid fuel by hydrogenation of coal (Bergius and related processes), and on the gasification of coal in a vortex reactor has led to developments of theoretical as well as practical importance.

Synthesis of Liquid Fuels from Hydrogen and Carbon Monoxide
(Fischer-Tropsch and Related Processes)

Process Development

Pilot-Plant Operations

In the oil-circulation process that has been studied in the pilot-plant stage at the Coal-to-Oil Laboratories of the Bureau of Mines, a mixture of carbon monoxide and hydrogen (synthesis gas) flows upward through the converter, concurrently with the circulating oil, and the synthesis takes place in the expanded (by the flowing oil) bed of catalyst. The heat of the exothermic reaction is transferred to the cooling oil, so that no internal cooling surfaces are needed. Up to now, this process has been carried out in small pilot plants. This year, a barrel-per-day unit has been put into operation (see fig. 28). No unusual difficulties were experienced in running this plant, which is about 13 times larger than those previously used.

To fill the converter to a height of 8 feet, 307 pounds of synthetic-ammonia-type fused catalyst were reduced with hydrogen in two batches. After 98-percent reduction, the catalyst was stored under a low-boiling fraction of synthetic Diesel oil for about one-half year. Induction, which normally requires about 4 days, took 6 days because of trouble with the carbon dioxide-absorption system. When synthesis was started at 254° C., 70 percent conversion was attained at about 450 p.s.i.g., an hourly space velocity of 600 of fresh 0.7H₂:1CO synthesis gas, and a gas recycle ratio of 1:1. A decrease in the activity of the catalyst after about 1 week of synthesis probably was caused by relatively large amounts of carbon dioxide in the recycle gas. Installation of a more efficient scrubber and re-reduction of the catalyst made resumption of the synthesis possible. The experiment was terminated after 677 hours. During the test, the usage ratio had increased to about 0.9H₂:1CO, the concentration of iron in the recycle oil had risen, and the average molecular weight of the product had increased.

A second experiment in the barrel-per-day plant, with 1H₂:1CO gas, lasted 1,245 hours. It was terminated because of disintegration of the catalyst, of which only about 45 percent had remained in the converter. The distribution of the liquid and solid hydrocarbons during steady state conditions was 62.4 percent gasoline, 13.9 percent Diesel oil, 10.6 percent heavy distillate, and 13.1 percent wax. After removal of the oxygenates and adjustment of the Reid vapor pressure, the gasoline had an octane number of 77 (unleaded) or 87 (3 cc. TEL added). The Diesel oil, boiling in the range 204°-285° C., had a pour point of 0° F. and a cetane number of 73, which exceeds the premium-grade specification of the Navy by about 20 numbers.

A smaller pilot plant was used to evaluate a fused catalyst, prepared at the Demonstration Plant at Louisiana, Mo., for use there. This catalyst was similar to the commercial synthetic-ammonia-type catalyst used extensively at the Bruceton Station. Initial tests seemed to indicate that the new preparation was not active enough, but subsequent runs showed that the catalyst had been poisoned by the sulfur compounds (fig. 29) in the petroleum fraction which was used as the cooling oil. Although the original petroleum fraction impaired functioning of the catalyst, the used petroleum fraction was not detrimental to the activity, probably because most of the sulfur had been removed in the first operation. When cooled with the used petroleum fraction or with synthetic oil, the catalyst made at the Demonstration Plant exhibited satisfactory activity and mechanical strength.

Laboratory-Scale Experiments

Catalyst-Oil Slurry Process

This process is similar to the oil-circulation process, in that the catalyst is suspended in oil. Unlike the latter process, however, the slurry operation involves use of a powdered catalyst. The modification of the process chosen as most suitable for bench-scale work employs no circulation of slurry outside of the reactor. A number of variables of this process were investigated during the year.

The activity of siderite was unsatisfactory, as only 20-percent conversion of the synthesis gas could be obtained at 300° C., at 100 to 300 p.s.i.g. pressure, and hourly space velocities ranging from 100 to 300.

Two experiments were made with precipitated-iron catalysts. In one run, the dry catalyst was subjected to a "typhoon" induction (high temperature and high space velocity of synthesis gas) in a fluidized reactor (see fig. 30) before synthesis. Synthesis was interrupted after more than 500 hours by mechanical failure, after it had been established that as much as 88 percent of the synthesis gas could be converted at 266° C., 150 p.s.i.g., and an hourly space velocity of 150. Production of undesirable gaseous hydrocarbons was quite low.

The second experiment was begun by inducing the precipitated catalyst in the slurry phase. Synthesis was begun at 100 p.s.i.g. and 253° C. When the pressure was raised to 150 p.s.i.g., the temperature could be lowered by about 30° C. while the conversion was maintained essentially constant. A subsequent increase of the temperature effected almost 90-percent conversion of the synthesis gas. Most of the increased conversion resulted in the production of hydrocarbon gas. A study of the effect of space velocity on the product distribution during this experiment showed that the formation of hydrocarbon gas is not so much a function of temperature as it is of the amount of conversion: At a given temperature, less gas was produced as the extent of conversion was decreased by increasing the space velocity of the synthesis gas.

The difficulties initially experienced with settling of fused catalysts have been overcome. To keep the catalyst suspended in the slurry, a suspension aid - modified bentonite - was added to the oil, producing a gel of higher

viscosity than that of the normal slurry. It was thus possible to make uninterrupted experiments for 2 and 3 months. About 75 percent of the oil product boils in the gasoline range, and less than 5 percent is wax. During the first 2,000 hours of one test, for example, about 476 pounds of liquid and solid hydrocarbons and an estimated 28 pounds of oxygenated compounds were synthesized per pound of iron; of the hydrocarbons, 79 percent were in the gasoline range, 13 percent were Diesel oil, and only 2 percent were waxes.

High-Pressure Fixed-Bed Process

The effect of pressure (in the range of 500 to 1,500 p.s.i.g.) on the synthesis reaction was studied with fused iron catalysts (see figs. 31 and 32) that had been nitrided and treated with synthesis gas at high space velocities and lower pressures to avoid the possible clogging of the outlet of the reactor by ammonium carbonate. In one such experiment, the iron carbonitride was used initially at 500 p.s.i.g. and 206°-208° C. After 45 days, during which the pressure was varied between 500 and 1,500 p.s.i.g., a steady synthesis temperature of 241°-242° C. was attained for about 60 percent conversion of the 1.LH₂:1CO gas (usage ratio, 0.72-0.75). Comparison with a test at 300 p.s.i.g. showed that the approach to steady-state conditions was apparently independent of pressure. The pressure dependence of the rate of synthesis was found by varying the hourly space velocity (172 to 411) to maintain otherwise constant conditions. This function is expressed by

$$r = k p^{\alpha} ,$$

where r = reaction rate (cc./hr.), k = specific reaction-rate constant, p = absolute pressure (p.s.i.), and α = pressure coefficient. While α has previously been found to be about unity in the pressure range 100-300 p.s.i.g., it was 0.72 between 500 and 1,500 p.s.i.g. The effect of pressure on the distribution of products was rather small. As is usual with fused iron carbonitride catalysts, the percentage of oxygenated products was high but did not change markedly with pressure. There was a slight tendency toward production of less methane and more liquid material at higher pressures. At the same time, the average molecular weight of the liquids and waxes appears to have been lowered somewhat by raising the pressure. Further tests are in progress to study the effect of pressure on synthesis with reduced fused catalysts.

Catalyst-Activity Tests

Of the factors that determine the quality of a gas-synthesis catalyst, origin, and storage and pretreatment effects were studied (fig. 33). A commercially available iron fluoride showed no activity. A low-cost iron ore was active but produced so much methane as to be worthless for the synthesis of liquid fuels. Several catalysts were prepared from mixtures of magnetite, potassium carbonate, and ball clay in different proportions. These catalysts had high mechanical strength but operated at relatively high temperatures and in most instances produced predominantly gaseous hydrocarbons. After nitriding, one of these preparations operated 20° C. lower than previously (for the same contraction) and produced 20 percent more gas.

The effect of storage under oil on the activity and selectivity of a synthetic-ammonia-type catalyst was negligible for storage periods as long as 6 months. No difference was found between the storage qualities of crude synthetic oil (made with an iron catalyst) and of oil washed with caustic to neutralize any acid, washed with water to remove the caustic, and dried to produce a dry, neutral oil.

Cementite was prepared by four different methods, using a fused catalyst, and the effect of the method of preparation on the synthesis was investigated. Partial carburization of the iron to Hägg carbide and subsequent homogenization (cementite formation) by annealing produced the most active of these catalysts for use at 100 p.s.i.g. pressure. Direct formation of cementite by carburization with methane and annealing to cementite of a mixture of Hägg carbide and metallic iron in a used catalyst yielded catalysts of lower activity. However, the presence of magnetite in the used catalyst may have had an unfavorable effect. At 300 p.s.i.g. there was no appreciable difference in activity between cementite prepared by homogenization of a mixture of Hägg carbide and metallic iron and cementite made by "typhoon" induction (see Catalyst-Oil Slurry Process).

The activities of reduced, normally inducted, and "typhoon" inducted, precipitated catalysts were also compared. "Typhoon" induction produced a remarkably active catalyst. This enhanced activity may be due in part to increased surface resulting from mechanical disintegration of the catalyst during its induction. The production of gaseous hydrocarbons was very low.

Reaction Mechanism Studies

Catalyst Composition and Reactivity

Further studies were made of the chemical properties of iron carbides, which, while not necessarily catalysts themselves, are always formed as by-products of the synthesis and appear to have a profound effect on the activity of iron catalysts. The rate of carburization with carbon monoxide of two widely different types of catalyst obeyed the equation

$$-d(\text{Fe})/dt = k(\text{Fe})^2$$

at least up to about 50 percent carbiding and at gas velocities where transport cannot be a limiting factor; here t = time, k = specific reaction-rate constant, and (Fe) = mole fraction of metallic iron remaining. This rate law permitted determination of the temperature and pressure dependence of the initial rate of carburization. The activation energies varied between 27 and 32 kg.-cal. per mole, and the exponential factors for the pressure dependence varied between 0.2 and 0.3, depending on the catalyst.

The effect of alkali on carburization of reduced iron catalysts over a range of alkali concentrations and carburization temperatures was to decrease the rate of carbide formation (at least after about 50 percent of the iron had been carburized), to increase the rate of carbon deposition (after carburization was essentially completed), and to decrease the rate of reduction

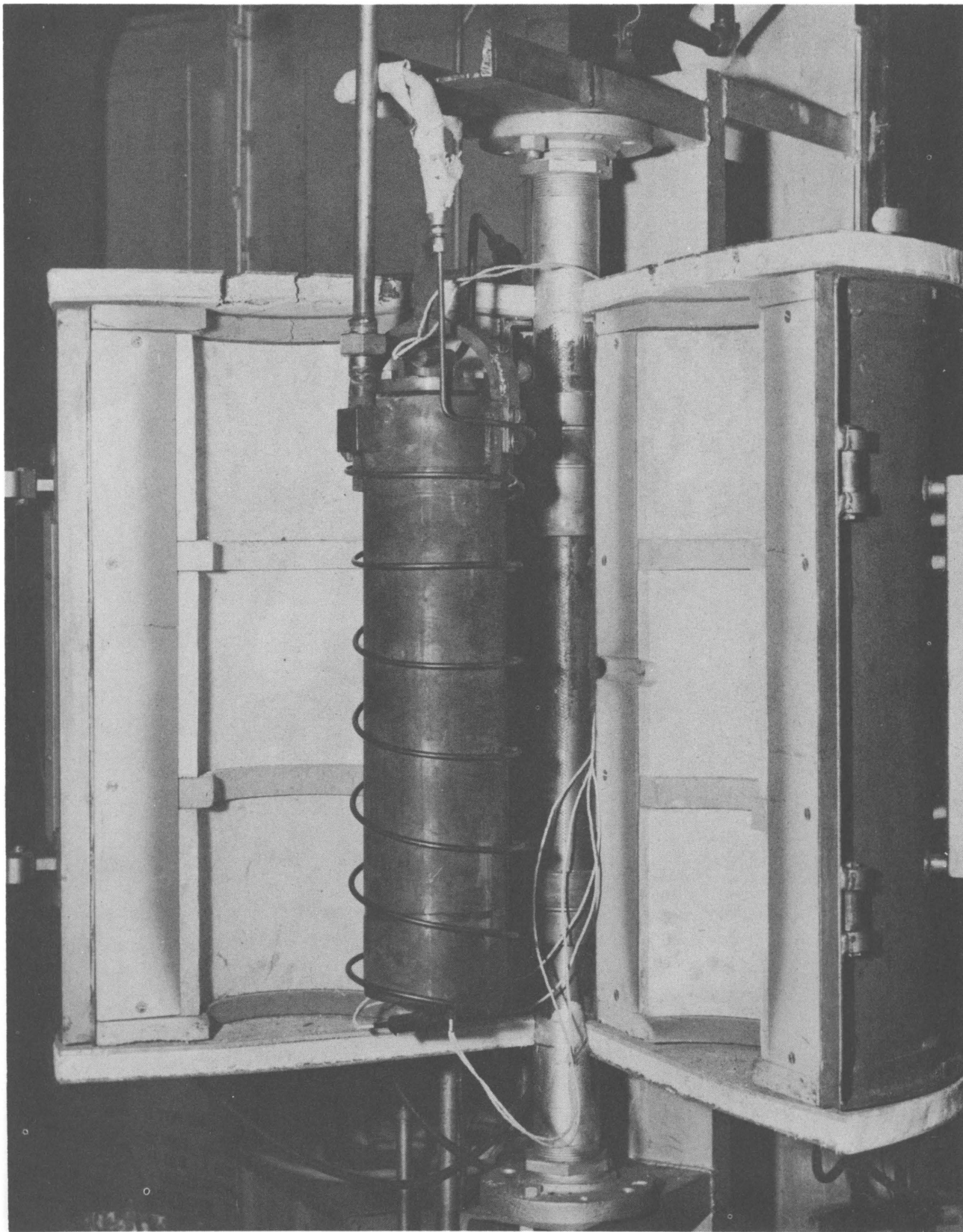


Figure 32. - Steel-shot oxidation unit.

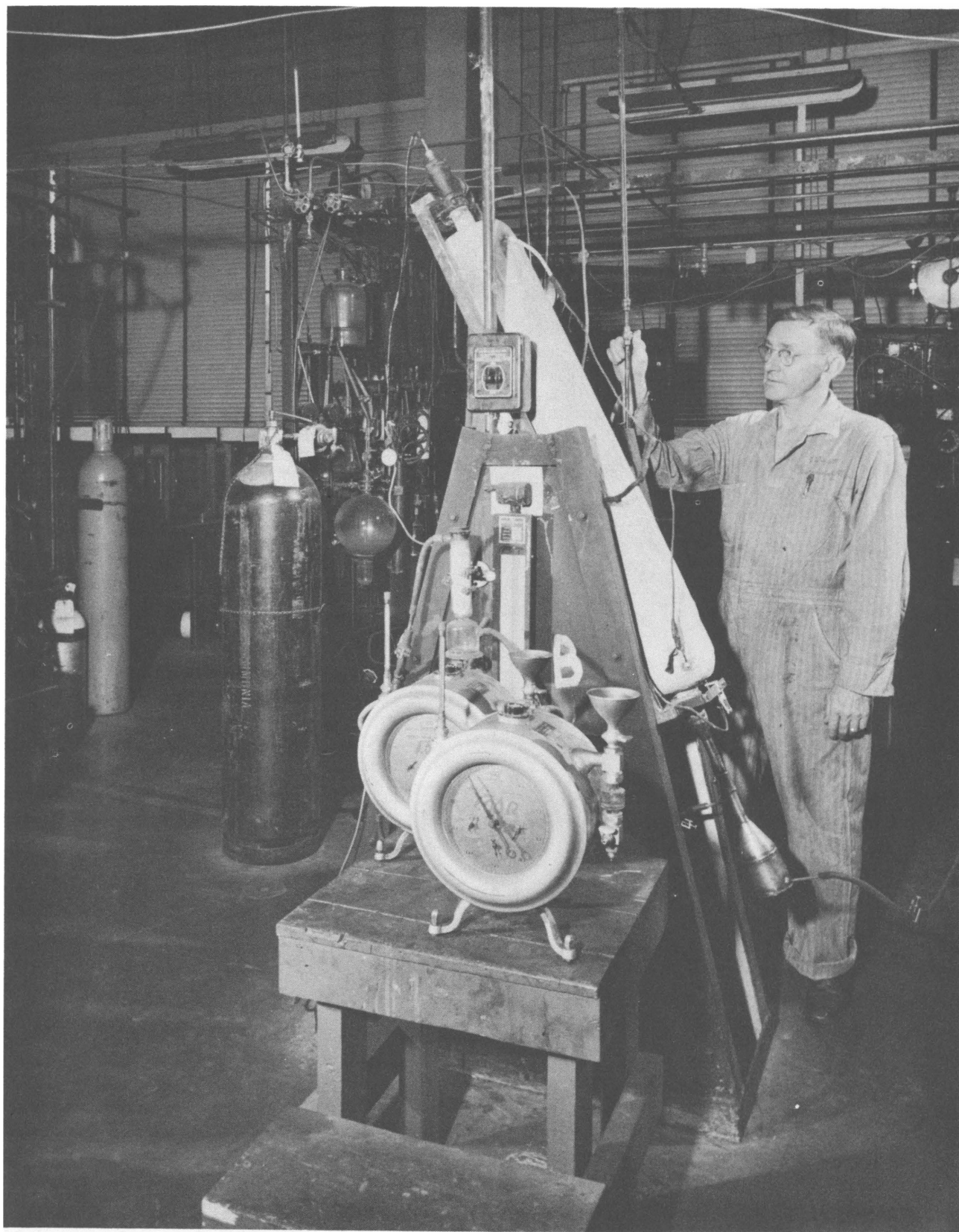


Figure 33. - Tilting reduction furnace.

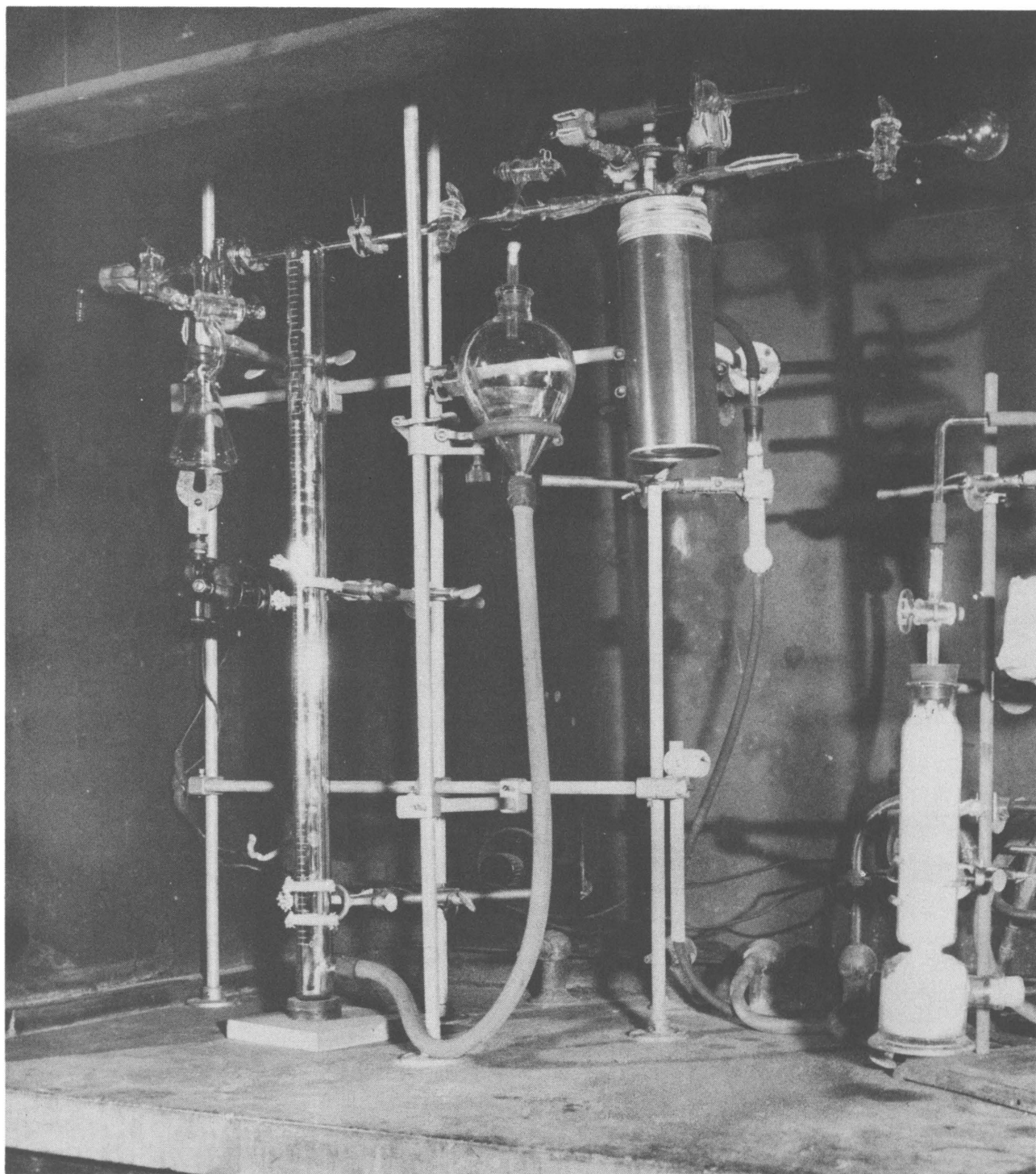


Figure 34. - Apparatus for measuring gas evolution.

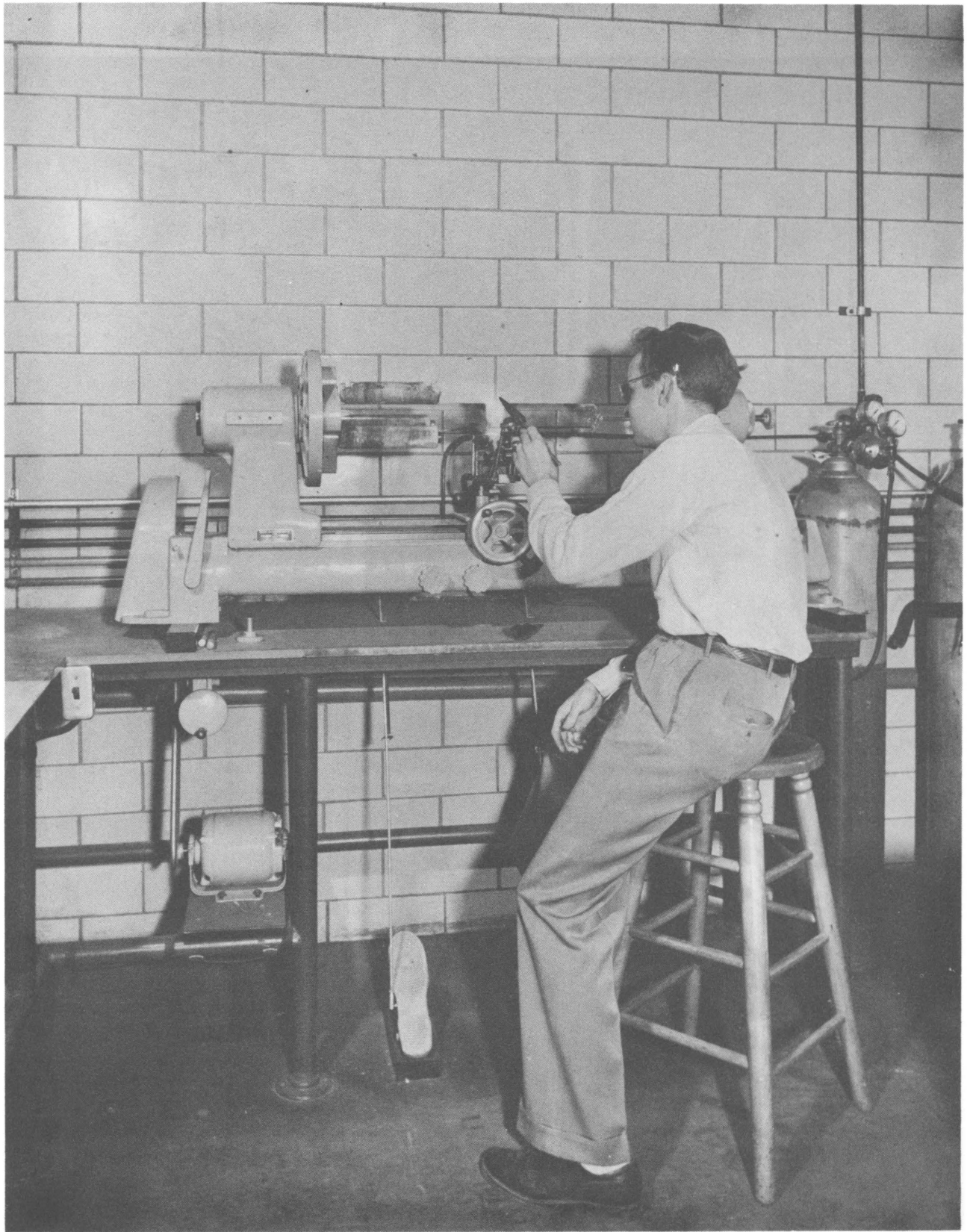


Figure 35. - Glass-blowing lathe.

of the carbide. Nitriding rates of similar reduced iron catalysts were also decreased when alkali was added to the catalysts. This effect may be due to partial covering of the surface by the promoter.

Carburization of reduced catalysts with synthesis gas of varying composition was found to lead to the formation of fairly pure Hägg carbide. Although small amounts of metallic iron may remain unreacted and although formation of magnetite is increased somewhat as the ratio of hydrogen to carbon monoxide increases, the rate of carburization is rapid, and the method is simple and may be more convenient than carburization with pure carbon monoxide, especially since gas mixtures are available for the synthesis in any case.

The formation of Hägg carbide from hexagonal close-packed iron carbide was characterized magnetically by the presence of two invariant Curie points. Because Curie points are quite sensitive to changes in composition and to the formation of solid solutions, this phenomenon is proof of the fact that the transition from one structure to the other was discontinuous; that is, that nuclei of the new phase grew at the expense of the old phase, that the compositions of the two carbides remained unchanged during the transformation, and that there either was no mutual solubility of the two carbides in each other or that equilibration was too slow to become noticeable. The rearrangement proceeded without an induction period in contrast to the reaction of Hägg carbide with metallic iron to form cementite, which takes place at higher temperatures. Considering reactions of iron carbides in the solid phase, free carbon appears to be formed from carbide only by the decomposition of cementite. As this reaction occurs at temperatures far above those used in the synthesis, carbon deposition during the synthesis cannot be accounted for on this basis by thermal decomposition of iron carbide.

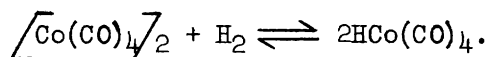
The reduction with hydrogen of Hägg carbide and of cementite is preceded by an induction period, after which the rates of reduction of the two carbides are essentially constant. This conclusion was reached from a study of magnetite, which was freed of alkali, reduced, and carburized - partly to form cementite (by annealing of Hägg carbide and free iron) or fully to form Hägg carbide.

One of the main causes for failure of a catalyst during synthesis is its mechanical disintegration, resulting from oxidation and simultaneous carbon deposition. To determine its susceptibility to oxidation, Hägg carbide was used in the synthesis at pressures ranging from 100 to 300 p.s.i.g. Up to an atom ratio of 0.15 of oxygen to iron, no significant effect of pressure was found on the rate of oxidation. At higher ratios, however, oxidation increased markedly with pressure. When the pressure was maintained constant and the temperature was varied between 240° and 255° C., a similar effect was observed, an increase in temperature of 15° C. being equivalent to an increase in pressure of about 50 pounds. Deposition of free carbon was rapid during the first few days of synthesis but stopped after some time.

Oxo Reaction

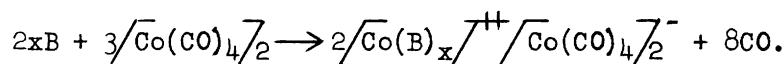
Reactions similar to those occurring in the oxo synthesis occur also in the Fischer-Tropsch process. In the oxo reaction, carbon monoxide and hydrogen

combine with olefins or alcohols to produce oxygenated compounds of higher molecular weight than the starting materials. Cobalt usually is the catalyst, probably in the form of cobalt hydrocarbonyl, $\text{HCo}(\text{CO})_4$, which may be formed from dicobalt octacarbonyl under synthesis conditions according to the equation

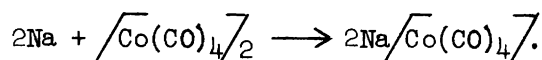


Although cobalt hydrocarbonyl can be prepared directly, it is difficult to keep as it becomes unstable above -33°C . The storage problem was partly overcome by collecting the acid in toluene and storing it in an atmosphere of carbon monoxide. Under these conditions, only very little decomposition was observed at room temperature during 24 hours (fig. 34). Methods were developed for the analysis of mixtures of cobalt carbonyl and hydrocarbonyl. A considerable amount of cobalt hydrocarbonyl was found in the reaction product from cobalt carbonate, benzene, and synthesis gas.

The formation of complexes of dicobalt octacarbonyl with organic compounds has previously been explained as a displacement of 1 or more moles of carbon monoxide by the entering organic molecule. This view has been shown to be untenable. Instead, the organic molecule effects a disproportionation of the dicobalt octacarbonyl into cobalt ion and cobalt carbonyl anion according to the generalized equation



The electrons necessary for the formation of the anion may be derived from some of the cobalt or from an external source. The tendency to form the stable cobalt carbonyl anion (rare-gas structure) is probably the driving force for the reactions. Addition of electrons from an external source is illustrated by the reaction of sodium with dicobalt octacarbonyl:



A study is being made of the effects of contact time, temperature, catalyst concentration, and pressure on typical oxo reactions.

Characterization of Synthesis Products

Analyses

The total liquid product obtained from hydrocarbon synthesis over a nitrided-iron catalyst at 240°C . and 20 atmospheres pressure was separated into fractions by a scheme involving several distillations, extractions, and phthalation, and the fractions were analyzed by chemical and spectrographic methods (figs. 35-37). A new mass spectrometric method was developed to determine the higher alcohols in this product. The total aqueous phase represented 26.1 percent of the condensed product. Some of its components and their amounts are shown in table 15; alcohols were predominant, and ethyl alcohol was by far the largest constituent of this phase. The oil phase, 73.9 percent of the condensed product, contained more than 45 percent of oxygenates, chiefly alcohols but also significant amounts of esters. The hydrocarbons were predominantly saturated. More than 80 percent of the oil phase boiled between 50° and 350°C ., and a detailed analysis of this part of the product is given in table 16.

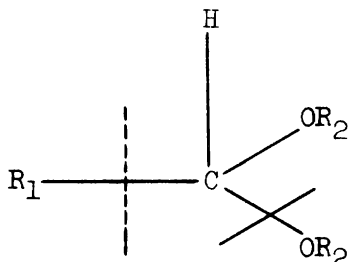
TABLE 15. - Some oxygenated substances in condensed product of Fischer-Tropsch synthesis over nitrated catalysts

Component	Composition concentration by weight, percent, of			Fraction of total component in aqueous phase
	Oil phase	Aqueous phase	Total	
Acids.....	-	5.28	1.38	-
Acetone.....	-	.12	.031	-
Methyl ethyl ketone.....	-	.09	.023	-
Methyl propyl ketone.....	-	.06	.016	-
<u>Alcohols</u>	20.46	14.32	18.84	0.198
Methanol.....	.06	.51	.18	.66
Ethanol.....	5.70	11.53	7.22	.417
n-Propanol.....	3.28	1.51	2.81	.140
i-Propanol.....	.08	-	.06	-
n-Butanol.....	2.85	0.48	2.23	.056
i-Butanol.....	.01	-	.008	-
n-Pentanol.....	2.29	.23	1.76	.034
n-Hexanol.....	1.89	.06	1.41	.011
n-Heptanol.....	1.54	0	1.14	0
n-Octanol.....	.95	0	.70	0
n-Nonanol.....	.63	0	.47	0
C ₁₀ and higher alcohols...	1.18	0	.87	0
Total identified oxygenates	20.46	19.87	20.29	0.26

TABLE 16. - Chemical composition of oil fraction boiling from 50° to 350° C. from nitrated catalyst

	Fraction number			
	2	3	4	(2-4)
Boiling range, °C.....	50-150	150-250	250-350	50-350
Components, weight, percent:				
Total oil.....	51.95	17.06	13.60	82.61
Hydrocarbons.....	17.6	38.4	8.0	20.2
Double bonds				
Total α	4.1	5.0	.8	3.6
Total β	2.4	.6	1.4	1.8
Hydrocarbon α	2.28	2.28	0	1.9
Hydrocarbon β09	.22	0	.1
Hydrocarbon branched- α13	.06	0	.1
Carboxyl (acid).....	.6	1.6	0.2	.8
Carboxyl (ester).....	3.4	5.0	10.4	5.0
Carbonyl.....	2.0	1.1	1.1	1.7
Hydroxyl.....	10.6	3.5	.3	7.4
Acid in fraction.....	1.2	15.2	1.0	1.9
Acid in total oil.....	0.6	.9	.1	1.6
Ester in fraction.....	6.8	16.4	50.4	14.8
Ester in total oil.....	3.5	1.8	6.9	12.2
Aldehyde and ketone in fraction....	5.1	5.0	7.9	5.6
Aldehyde and ketone in total oil....	2.6	.9	1.1	4.6
Alcohol in fraction.....	46	27	3.5	35.2
Alcohol in total oil.....	24	4.6	.5	29.1
Oxygenated compounds in fraction....	59.1	53.6	63.1	57.5
Oxygenated compounds in total oil...	30.7	9.1	8.6	48.4

By means of new methods developed with the mass spectrometer, other constituents in the liquid Fischer-Tropsch product can be identified. These are the acetal-type compounds,



in which R_1 is H for formal, CH_3 for acetal, C_2H_5 for propional, etc. In analogy to the mass fragmentation of simple ethers, one may expect the C-O bond to rupture most easily (as indicated by the solid line), and the C- R_1 bond not quite as readily (shown by the dashed line). The resulting mass fragments are distinguishable because of the mass difference between C and O. The spectra of several formals, acetals, and propionals exhibited odd mass peaks that could be correlated by a simple empirical equation which may be used to predict the positions of corresponding mass peaks for the acetals of higher aldehydes. This correlation is applicable also to certain compounds related to acetals, such as dioxolanes. It shows, furthermore, that no acetal-type compound can have a mass peak of 61, which occurs commonly in mixtures of oxygenated compounds. This odd peak may be attributable to hemiacetals.

Product and Isomer Distribution in the Hydrocarbon Synthesis

Schemes for predicting the isomer distribution of each paraffin hydrocarbon were developed some time ago at the Bruceton laboratories. These schemes are based on a few simple rules for chain growth and are in satisfactory agreement with actual isomer distributions as determined in the products from iron and cobalt catalysts. A similar scheme, accounting for the carbon-number distribution of the hydrocarbon product, was available but not easily applicable because fractionation of the hydrocarbons into close cuts was required. Further development of this method has made it applicable to relatively crude fractionation data, and agreement of theory and practice permits some valuable conclusions concerning the mechanism of the synthesis. The method is based on the assumption that chain growth in the synthesis proceeds by stepwise addition of single carbon atoms and that the probability of growth, ∞ , of a given hydrocarbon chain is independent of the carbon number above C_5 , although it may vary with experimental conditions. Agreement of data and theory is illustrated in figure 38, where product distribution is plotted as a function of the probability of growth. This graph is of practical interest, as it shows that not more than about 30 percent of the total liquid and solid product can be expected to be in the range of Diesel oil. Furthermore, this amount of Diesel oil should be readily obtainable, because the maximum yield of the fraction remains nearly unchanged over a rather wide range of probabilities of growth, that is, conditions of operation of the synthesis. As a matter of fact, attempts made in other laboratories to increase the yield of Diesel oil obtained in the gas synthesis process have been unsuccessful.



Figure 36. - Glass-blowing shop.

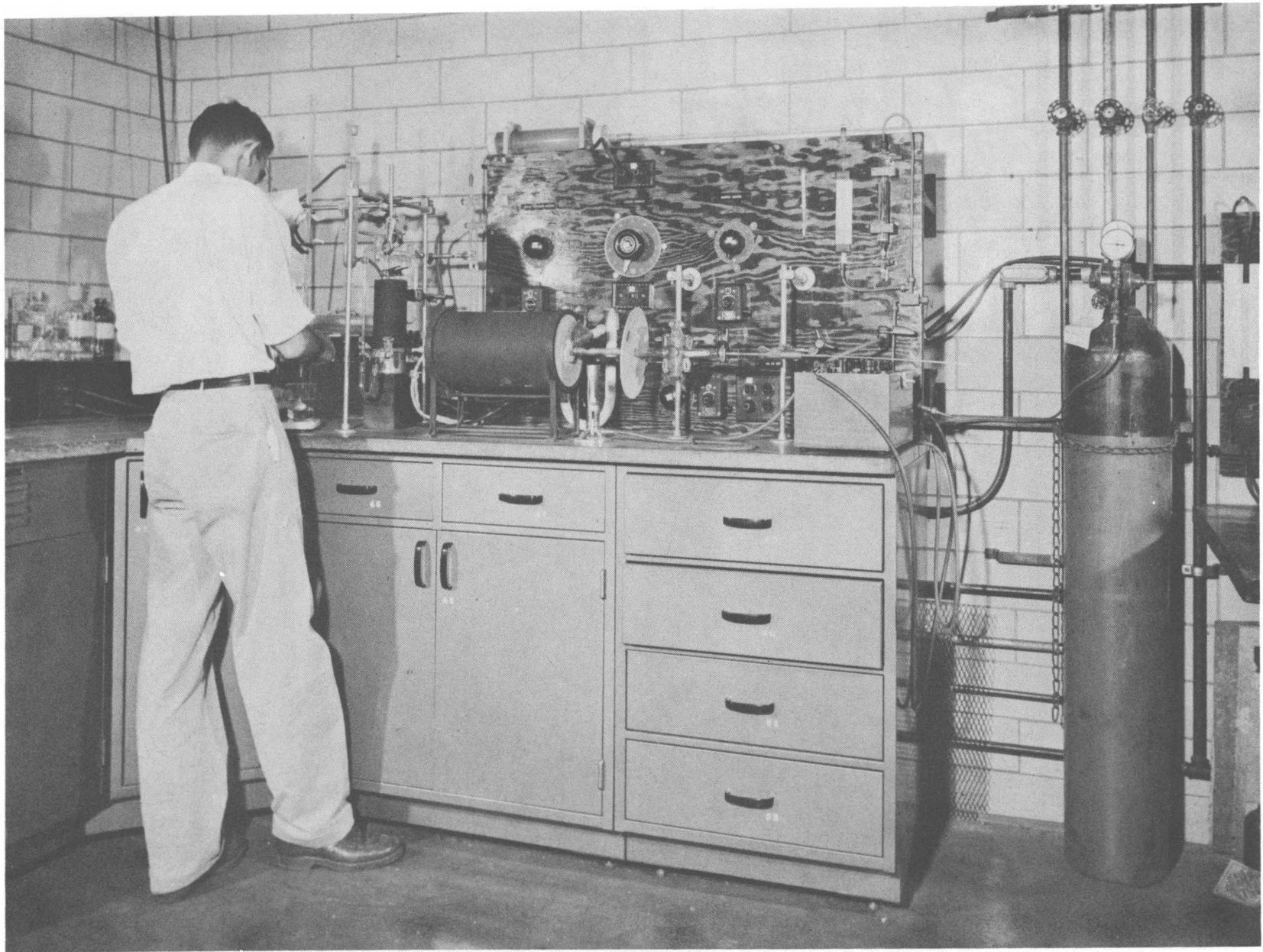


Figure 37. - Modified Unterzaucher apparatus for direct determination of oxygen.

Synthesis of Liquid Fuels by Hydrogenation of Coal

Process Development

Fluidized-Bed Hydrogenation

The possible advantages of hydrogenating coal in a fluidized bed (see fig. 39) instead of in the liquid phase have been mentioned in the previous annual report. This year's studies were concerned with finding conditions under which a continuous fluidized process is operable, and especially with developing a method of operation that would avoid agglomeration of the fluidized mass. Two small units were used for this purpose; in one, the coal was heated to reaction temperature in 1 to 2 hours and kept at that temperature for a certain time. In the second unit, coal was charged only after the reaction temperature and the rate of flow of hydrogen had been established. The coal was thus heated to reaction temperature in less than 10 minutes, and the temperature was permitted to rise (by as much as 100° C.) depending on the amount of energy liberated during the hydrogenation.

From the experience gained with these units, the following conclusions were drawn: Slow heating of the fluidized coal without catalyst permits removal of the liquid products by the fluidizing gas at a rate rapid enough to prevent agglomeration. Addition of a catalyst accelerates the hydrogenation under otherwise equal conditions to a point where the heavy oil acts as a binder for the coal particles, and subsequent coking of the solid results in agglomeration. Rapid heating of the coal to less than 400° C. does not lead to agglomeration because the oil can be removed as rapidly as it is formed. Rapid heating of a very reactive coal to 500° C. or higher also results in satisfactory operation. In this case, the heat of reaction raises the temperature of the coal particles so that any liquid that remains on them is carbonized and agglomeration is prevented. If the coal is not reactive enough, or if an inert diluent (ash) absorbs the heat of the reaction, agglomeration may occur.

Thus, a continuous unit should be operable below about 400° C., or at high enough temperatures to carbonize any liquid not removed from the coal particles by hydrogen. Construction of such a pilot plant has been completed. It is operable up to 700° C. and permits a contact time of 6 minutes at a rate of flow of 5 pounds of coal per hour. The reactor consists of a 1-inch pipe provided with a screw feeder at the bottom, a 3-inch pipe separator at the top, and a 1-inch external standpipe leading to pressurized receivers. Gases and vaporized liquids pass overhead from the separator through a stainless-steel filter into the product-recovery system, while the char falls by gravity through the standpipe into the receivers.

Bench-Scale Studies

Hydrogenation of Various Coals

The objectives of the study of the Bergius-I.G. coal-hydrogenation process during the past year were determination of the suitability of various coals, of the applicability and activity of a number of catalysts, and of the kinetics of the hydrogenation process.

A blend of Western Kentucky coals was found to be suitable for use by the Demonstration Plant at Louisiana, Mo. Hydrogenation with impregnated ferrous sulfate catalyst at 450° to 475° C. and 700 atmospheres gave satisfactory results. A sample of Illinois No. 6 coal, Darmstadt No. 1 mine, Marissa, St. Clair County, Ill., was hydrogenated successfully at the same pressure, after neutralization of the alkaline ash with sulfuric acid and impregnation with ammonium molybdate as catalyst. When hydrogenated at about 250 atmospheres after impregnation with 1 percent of ferrous sulfate, its product distribution was similar to that obtained from the Kentucky coal blend.

Three coals were hydrogenated in a rotary autoclave at an initial pressure of hydrogen of 1,000 p.s.i.g., for 1 hour, at 450° C., and with or without a catalyst (1 percent tin plus 0.5 percent ammonium chloride). These coals came from Lake DeSmet Reservoir, Wyo.; Butte Valley Co., Huerfano County, Colo.; and Baldy Coal Co., Las Animas County, Colo. The results obtained with these coals are compared in table 17 with those obtained with coal from the Bureau's Experimental Mine, Bruceton, Pa.; Rock Springs coal, D.O. Clark Mine, No. 9 bed, Superior, Wyo.; a blend of Western Kentucky coals, obtained from the Demonstration Plant, Louisiana, Mo.; and Beulah lignite, Beulah mine, Mercer County, N. Dak. The Lake DeSmet coal samples correspond to the 60- to 100- foot, 100- to 140- foot, and 140- to 180- foot layers in the coal vein. The DeSmet, Butte, and Baldy coals had high ash contents as received and would be more suitable for hydrogenation after removal of ash and moisture.

An extensive study was made on the Rock Springs coal to determine the effectiveness of various catalysts in the range of 425° to 485° C. and at an initial pressure of 3,700 p.s.i.g. of hydrogen. Iron, nickel, molybdenum, tin, and zinc were used in different forms and ranges of concentration. The most important criterion in the evaluation of these catalysts was the yield of hexane-soluble oil which is the most desirable product. Nickel and molybdenum, impregnated on the coal, were the best catalysts from that point of view. Economically, the use of 0.1 percent of nickel (impregnated as nickel chloride in these tests) appears preferable because it produced large amounts of oil and small amounts of gaseous hydrocarbons and is cheaper even than impregnation of 0.5 percent of iron as ferrous sulfate.

Rock Springs coal was used to determine the effect of the initial pressure of hydrogen upon the extent of liquefaction of the coal at 450° C. No effect was noticed for a contact time of up to 7 minutes. After 14.5 minutes, however, increased pressure of hydrogen (in the range of 500 to 2,000 p.s.i.g.) resulted in a reduction of the amount of benzene-insoluble material. It appears that, after 14.5 minutes, thermal cracking of the coal had proceeded to such an extent that stabilization of the unsaturated fragments had become dependent upon the partial pressure of hydrogen.

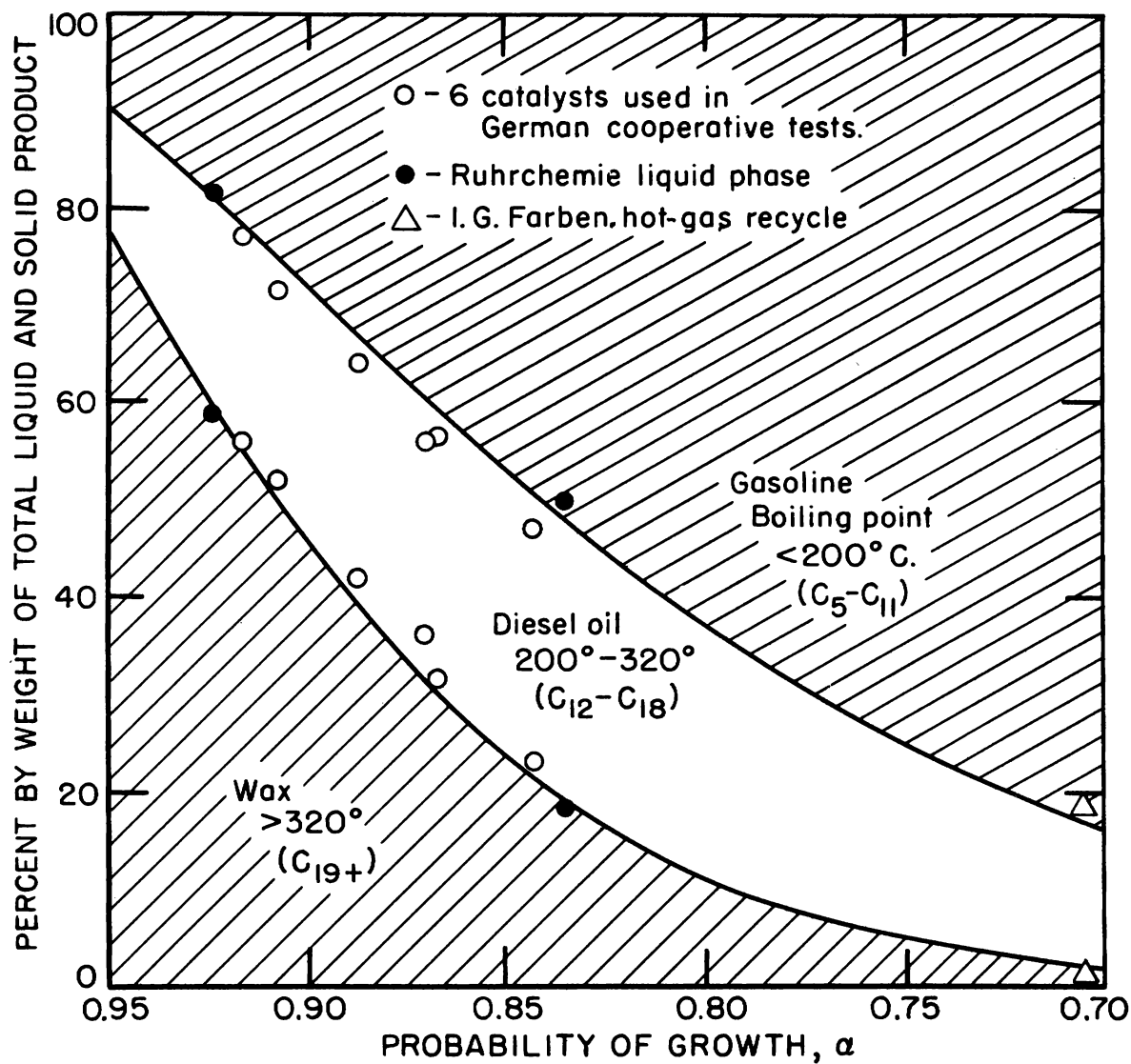


Figure 38. - Correlation of theoretical and observed product distributions of liquid and solid Fischer-Tropsch hydrocarbons obtained with iron catalysts.

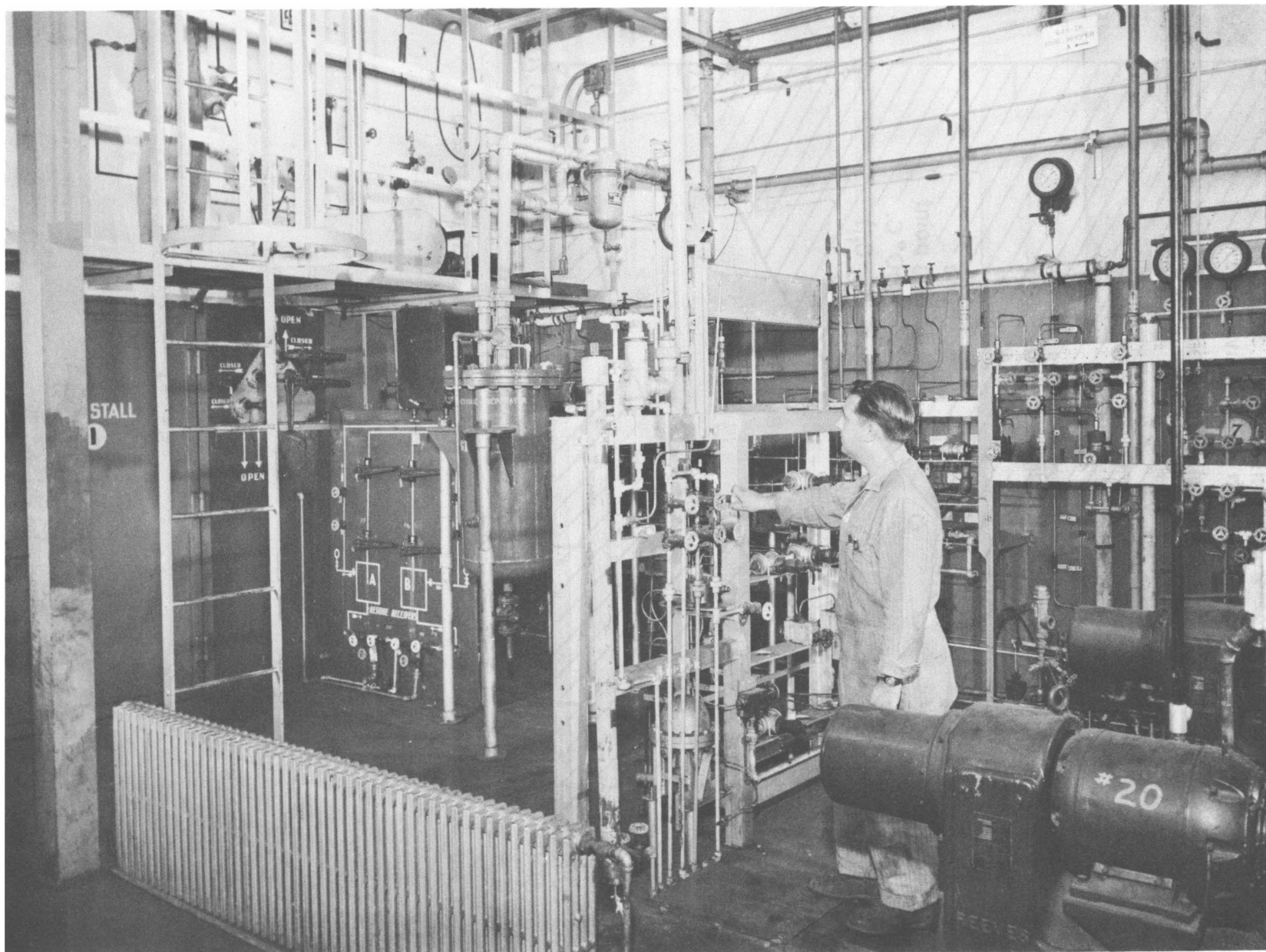


Figure 39. - Fluidized coal-hydrogenation unit.

TABLE 17. - Product distribution (weight percent; m.a.f. basis) from hydrogenation of various coals (without vehicle) for 1 hr. at 450° C. and 1,000 p.s.i.g. initial hydrogen pressure.

Test No.	Coal	Catalyst	Benzene-insolubles	Asphalt	Oil	Gaseous hydrocarbons	CO ₂	H ₂ O	H ₂ consumed
986	Bruceton	1 percent Sn + 0.5 percent NH ₄ Cl	12.99	43.02	27.99	12.51	0.65	5.9	4.37
1230	Rock Springs	do.	12.86	32.80	26.64	17.23	2.90	11.28	4.74
1719	Kentucky	do.	9.84	46.00	23.09	14.66	.33	7.72	4.34
1218	Beulah lignite	do.	43.27	13.60	19.90	11.60	9.00	11.88	3.65
	Lake DeSmet								
1767	60-100 feet	do.	18.35	26.01	16.88	17.70	9.02	15.87	4.61
1770	100-140 feet	do.	14.18	39.82	20.04	15.35	8.77	16.52	4.58
1805	140-180 feet	do.	27.61	18.85	16.17	15.07	9.30	16.48	4.29
1778	Baldy	do.	18.96	42.21	21.41	15.29	.15	5.26	3.94
1829	Butte	do.	42.71	13.22	19.61	15.31	2.73	9.74	3.66
1623	Bruceton	None	53.08	16.47	11.36	13.13	.61	6.98	2.57
1228	Rock Springs	do.	66.64	7.70	5.90	8.44	3.48	8.44	1.48
1216	Beulah lignite	do.	51.12	8.5	11.18	11.5	10.34	10.32	2.37
	Lake DeSmet								
1765	60-100 feet	do.	47.54	9.57	9.31	12.16	9.88	12.58	2.65
1768	100-140 feet	do.	52.79	6.47	6.13	13.70	9.80	13.06	2.69
1772	140-180 feet	do.	43.5	11.72	6.26	13.84	10.27	13.54	3.12
1775	Baldy	do.	73.48	7.99	4.30	9.48	1.06	4.25	.94
1833	Butte	do.	57.27	9.05	7.34	16.52	3.12	9.48	2.91

The pressure dependence in the range of 500 to 4,000 p.s.i.g. (initial pressure of hydrogen) of the hydrogenation reaction at 400° C. was determined with Rock Springs coal in two series of tests, one with tin and the other with molybdenum catalyst. Assuming that the amount of reaction was the same with both catalysts during the heating and cooling periods and allowing for the amount of reaction that takes place during these periods, straight lines were obtained when the logarithm of the amount of remaining benzene insolubles was plotted as a function of time. While the specific reaction rate constants thus obtained differed for the two catalysts, a plot of these constants as a function of pressure yielded identical slopes for both catalysts. The specific reaction rate constants are therefore a measure of the efficacy of the catalyst, and this method may be useful for quantitative evaluations of the activity of primary hydrogenation catalysts. Furthermore, the observed correlation of hydrogenation with pressure permits prediction of the yields over a range of pressures from only one experiment with any given coal, thus saving considerable time.

Hydrogenation and Coking of Oils Obtained from Coal

The production of gasoline by hydrogenation of coal necessitates catalytic splitting and hydrogenation of the middle oil, which is a product of the liquid-phase hydrogenation process. For this purpose, the Demonstration Plant has been using a German catalyst consisting of molybdenum, chromium, zinc, and sulfur on a clay support treated with hydrofluoric acid. Work has been started at the Coal-to-Oil Laboratories to duplicate or improve this catalyst, using a middle oil derived from a blend of Western Kentucky coal and the German catalyst for the orienting experiments. Removal of the primary gasoline, amounting to about 35 weight-percent of the middle oil, was advantageous because more gasoline was produced from the stripped oil, less hydrogen was consumed, and less hydrocarbon gas was generated. Furthermore, extraction of the gasoline preserved the phenols and cresols contained in it from (at least partial) destruction by high-pressure hydrogenation. After removal of the phenolic constituents, the primary gasoline had a motor octane number of about 73 and was therefore suitable as motor-gasoline stock. The secondary gasoline, derived from the hydrogenation product of the middle oil, had a motor octane number of about 79, irrespective of prior extraction of the oil.

The residual oil from coal hydrogenation (heavy-oil let-down or H.O.L.D.) is a mixture of oil and solids containing enough oil to remove the unreacted coal, ash, and catalyst from the plant. Recovery of the liquid fraction of this material is necessary for optimum utilization of the coal. The liquid consists of "oil," soluble in n-hexane; "asphaltene," insoluble in n-hexane but soluble in benzene; and benzene-insoluble material. One method of treating H.O.L.D. is steam stripping, and a continuous steam-stripping unit is illustrated in figure 40. Distilled water is pumped by a Zenith gear pump from the water supply bucket to the steam superheater, where it is heated by a 30-foot length of No. 14 (B. & S. gage) nichrome V wire. The superheated steam flows into the mixing block. A second Zenith gear pump moves the oil from a heated feed bucket through a preheater into the mixing block. Both pumps are operated from the same drive shaft and hence give a fixed steam:oil ratio. The

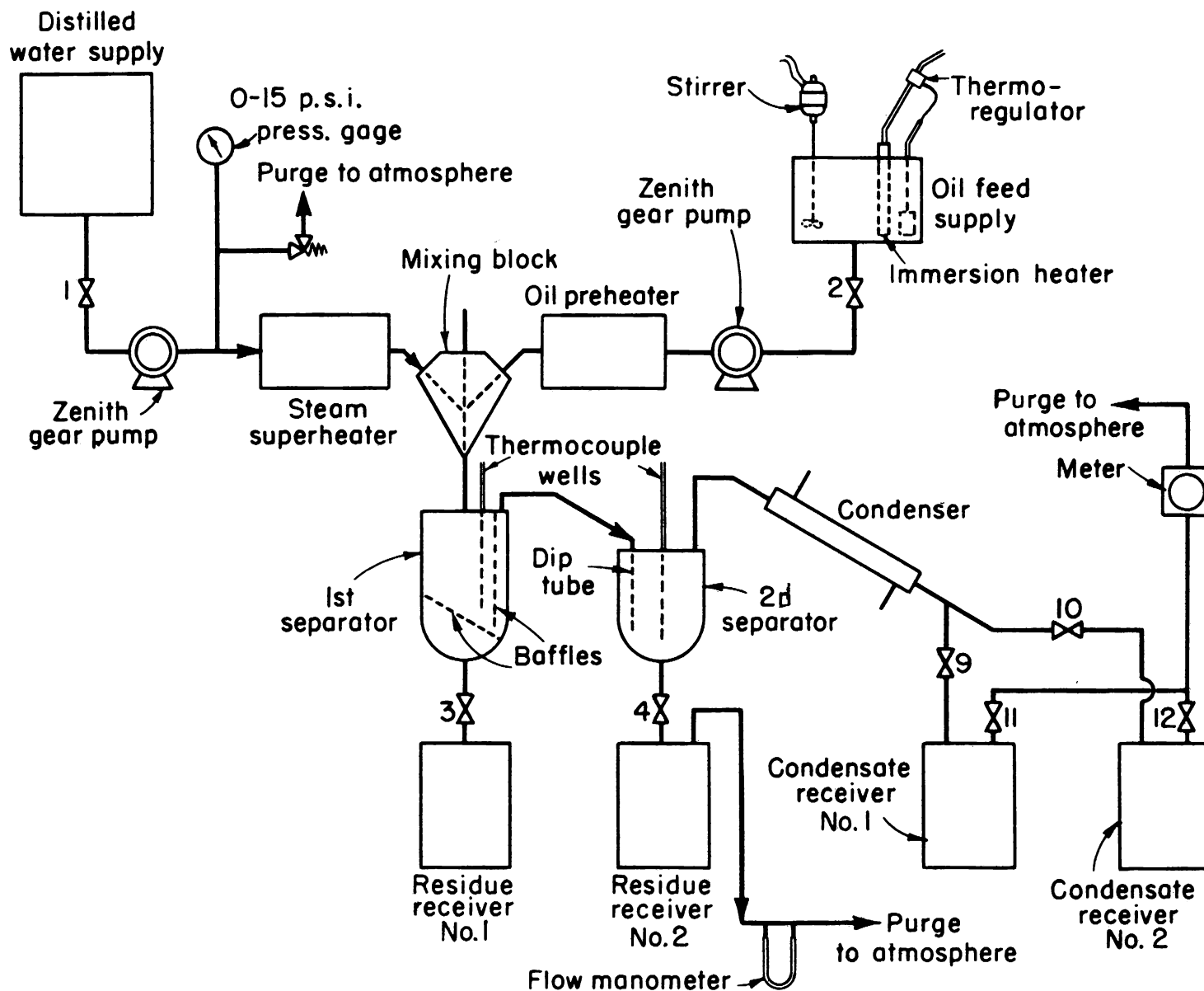


Figure 40. - Flow diagram of heavy-oil-let-down steam stripper.

mixture of oil and superheated steam enters the first separator, where benzene-insolubles and asphaltene residue are removed. The volatile materials pass into the second separator (held at a lower temperature) where heavy oils are separated. The lighter oils and steam pass overhead, then through a water-cooled condenser, and are collected in the condensate receivers. The noncondensable gases are metered and purged to the atmosphere. The condensed light oils and water in the condensate receivers are separated by decantation. The residue from the first separator and the oil from the second separator are withdrawn into receivers 1 and 2, respectively, through let-down valves. In this unit, an H.O.L.D. containing about 50 percent of n-hexane-soluble "oil" was separated into (1) a residue containing 99 percent of the benzene-insolubles and most of the ash, with an almost equal amount of "asphaltene"; and (2) a product containing 99.8 percent of the "oil," the remainder of the "asphaltene," and very little ash.

Another approach to the treatment of H.O.L.D. is coking. The effect of reaction temperature on the yield obtained during coking of H.O.L.D. was studied in the coking unit illustrated in last year's report. With unextracted H.O.L.D., the amount of distillate increased from 30 to 50 percent of the feed, while the content of benzene-insolubles in the residue rose from 60 to virtually 100 percent as the coking temperature was raised from 400° to 500° C. When the n-hexane-soluble "oil" was extracted from the H.O.L.D. and coked separately, the amount of gaseous product was smaller, and the recovery of distillate varied between 35 and 80 percent while benzene insolubles in the residue increased from 0 to 92 percent upon coking over the same temperature range. The "oil" fraction appeared to be the primary gas producer in H.O.L.D., 15 to 20 percent of the "oil" being converted to gas and benzene-insoluble material during coking. The behavior of the "asphaltene" and benzene-insoluble fractions during coking is under investigation. Knowledge of the product distribution obtained from these H.O.L.D. fractions will make possible the prediction of product distribution from coking of any H.O.L.D., provided its composition (in terms of these fractions) is known. Comparison of results obtained with the coking unit and those obtained with a commercial contact coking unit showed the results to be equivalent, so that the data obtained in this small unit will be useful for the design of a large coking unit that is to be built at the Demonstration Plant.

Characterization of Coal-Hydrogenation Products

Composition of Gasoline Obtained from Coal

A sample of gasoline produced by vapor-phase hydrogenation at the Demonstration Plant, Louisiana, Mo., was fractionated as follows:

<u>Boiling point, °C.</u>	<u>Weight, percent, of gasoline</u>
Below 50.....	8.8
50-150.....	66.3
150-185.....	18.2
Above 185.....	1.3
Volatiles and loss.....	<u>5.4</u>
Total.....	100.0

A major portion of the loss may be accounted for by dissolved gas, which was evolved during distillation. The fraction boiling at 50° to 150° C. was separated further into a paraffin-naphthene fraction; an olefin fraction, an aromatic fraction; and a fraction containing oxygen, sulfur, and nitrogenous compounds. The composition of this 50° to 150° C. cut is shown in table 18; and a further characterization by carbon number is given in table 19. This analysis was achieved by a long series of distillations, chromatographic separations, determinations of physical constants, and spectrometric analyses.

TABLE 18. - Composition of gasoline from Louisiana, Mo.

Component	Liquid-phase product, weight percent		Vapor-phase product, weight percent	
	50°-150° cut	Total product charged to v.p. unit	50°-150° cut	Total gasoline
Paraffins.....	17.42	-	18.92	66.31
Naphthenes - total.....	44.87	-	50.60	
Cyclopentane.....	.21	-	.34	-
Methylcyclopentane.....	<u>1/2</u> .26	<u>1/0</u> .271	<u>1/8</u> .51	<u>1/5</u> .65
Cyclohexane.....	<u>1/6</u> .80	<u>1/</u> .814	<u>1/3</u> .51	<u>1/2</u> .33
Dimethylcyclopentanes.....	2.83	.339	7.00	4.64
Methylcyclohexane.....	8.00	.958	6.95	4.61
Ethylcyclopentane.....	3.01	.361	5.12	3.40
C ₈ -naphthenes.....	11.01	1.319	10.30	6.83
C ₉ -naphthenes.....	6.63	-	8.86	-
Aromatics - total.....	21.06	-	27.50	24.74
Benzene.....	<u>1/1</u> .60	<u>1/0</u> .192	<u>1/6</u> .08	<u>1/4</u> .03
Toluene.....	6.93	.830	10.98	7.28
Ethylbenzene.....	7.31	.875	3.12	2.07
m.p. xylene.....	3.33	.399	6.16	4.09
o-xylene.....	1.81	.217	1.16	.77
150°	0	-	-	6.52
Olefins.....	9.57	-	1.1	1.4
Nonhydrocarbons.....	7.08	-	1.4	2.2
Unaccounted for.....	-	-	-	5.9
Benzene + potential benzene....	10.66	1.277	18.10	12.01

1/ Benzene plus potential benzene.

TABLE 19. - Composition of 50° to 150° C. cut of vapor-phase gasoline^{1/}

	Total	C ₅	C ₆	C ₇	C ₈	C ₉
Paraffins.....	20.62	-	7.80	6.14	4.37	2.31
Cyclopentanes.....	28.31	0.49	8.58	10.87	6.62	1.75
Cyclohexanes.....	20.08	-	3.57	6.15	6.56	3.80
Hydrindane.....	.13	-	-	-	-	.13
Aromatics.....	27.53	-	5.92	11.20	10.41	-
	96.67	0.49	25.87	34.36	27.96	7.99

^{1/} To put on basis of total gasoline, multiply by 0.6631.

Determination of Tar Acids and Bases

A blend of 21 percent gasoline, 11 percent naphtha, and 68 percent middle oil (the charging stock used for vapor-phase hydrogenation at the Demonstration Plant, Louisiana, Mo.) was examined for its tar-acid content. Half of this blend boiled below 250° C., and the tar acids were extracted with alkali from this fraction. Infrared spectrophotometric analysis showed the following percentages, based on the total amount of oil: 1.686 percent phenol, 0.724 percent o-cresol, 1.596 percent m-cresol, and 0.482 percent p-cresol.

Adaptation of a potentiometric titration method with antimony electrodes and ethylenediamine as the solvent has made possible direct determination of total tar acids in complex oils obtained by the hydrogenation of coal. This determination can be expressed in terms of the oxygen content, assuming that the oxygenates in the oils are monohydric phenols. The validity of this assumption was borne out by comparison of titrimetric data with ultimate analyses of an oil obtained by hydrogenation of Rock Springs coal.

A corresponding potentiometric titration method has been developed for estimating total tar bases in coal-hydrogenation oils. Glass and silver-chloride electrodes are used as indicator and reference electrodes, respectively, and perchloric acid in glacial acetic acid is the titrant. Phenols do not interfere with the analysis. Application of the method to oil obtained from Rock Springs coal showed about 70 percent of the nitrogen in the light and middle oils to be basic, while about 92 percent of the nitrogen in the naphtha fraction and about 30 percent of the nitrogen in the gasoline fraction were basic. Despite its high content of titrable nitrogen, only 40 percent of the nitrogen compounds of the light oil could be extracted with sulfuric acid, indicating the presence of high-molecular-weight and/or sterically hindered basic compounds.

Identification of individual tar bases up to quinoline was made for the tar-base fraction of the light oil obtained by hydrogenation of Rock Springs coal. A combination of analysis of the distillation curve of this fraction, ultraviolet and infrared absorption measurements, countercurrent distribution, neutralization equivalent determination, and formation of derivatives disclosed the presence of the following compounds: Beta- and gamma-picolines; 2,6-lutidine; aniline; o-, m-, and p-toluidine; 2,6-, 2,5-, 3,5-, and/or 2,4-xylydines; and quinoline. Although pyridine was not found, it was probably present

originally but lost in the plant by washing with water and during subsequent processing.

Countercurrent Distribution

The complex phenolic mixtures (tar acid) produced by hydrogenation of coal are composed largely of homologous and isomeric phenols, separation and identification of which are difficult or impossible by fractional crystallization and distillation. Because of their potential commercial value and the importance of oxygenated compounds in the study of the mechanism of the liquefaction of coal, characterization of these tar acids has practical as well as theoretical importance. By means of the countercurrent distribution technique, a mixture of closely related compounds is distributed between two immiscible solvents in successive countercurrent stages until separation of the components is achieved. The method is particularly useful for high-boiling compounds. Besides providing a means for separating such components, it may be used to check their purity, to calculate approximate ionization constants, and to obtain information on molecular structure (steric hindrance) and hydrogen-bonding.

Further development of the countercurrent-distribution method has led to a technique for measuring large (or small) partition coefficients. It consists of increasing the concentration of solute in the denser (or lighter) phase until measurable values are obtained. This method of "interchange extraction" was subjected to precise mathematical analysis, leading to an equation that related the partition coefficient to the number of extraction stages. The accuracy of the method was tested by determining the partition coefficients of o-phenylphenol in two systems.

The possibility of utilizing silver complexes of tar acids to aid in the countercurrent separation was studied with the three isomers of cresol. This method was found to be applicable only to a mixture of m- and p-cresol. Complex formation with cineole or with cineole and silver simultaneously was unsuitable for separation of the cresol isomers.

X-ray and Spectral Analyses

T.N.F. (2,4,7-trinitrofluorenone) forms brightly colored complexes of high and sharp melting points with polynuclear compounds. These complexes are easily purified by crystallization and readily decomposed into their original components, providing another tool for the separation of isomers. Furthermore, the crystalline complexes can be identified by their x-ray powder-diffraction pattern. Of 45 T.N.F. complexes thus examined, each had its characteristic pattern, completely different from those of its isomers and from the pure polynuclear hydrocarbons.

An infrared spectrometric (fig. 41) method for analyzing tar acids through the C_g group has been extended to include analysis of more complex mixtures of isomers. The method is applicable to determination of phenol plus the cresol isomers and to the cresols plus 2,4- and 2,5-xlenols; and only a crude separation of coal-hydrogenation oil into three fractions is now required.

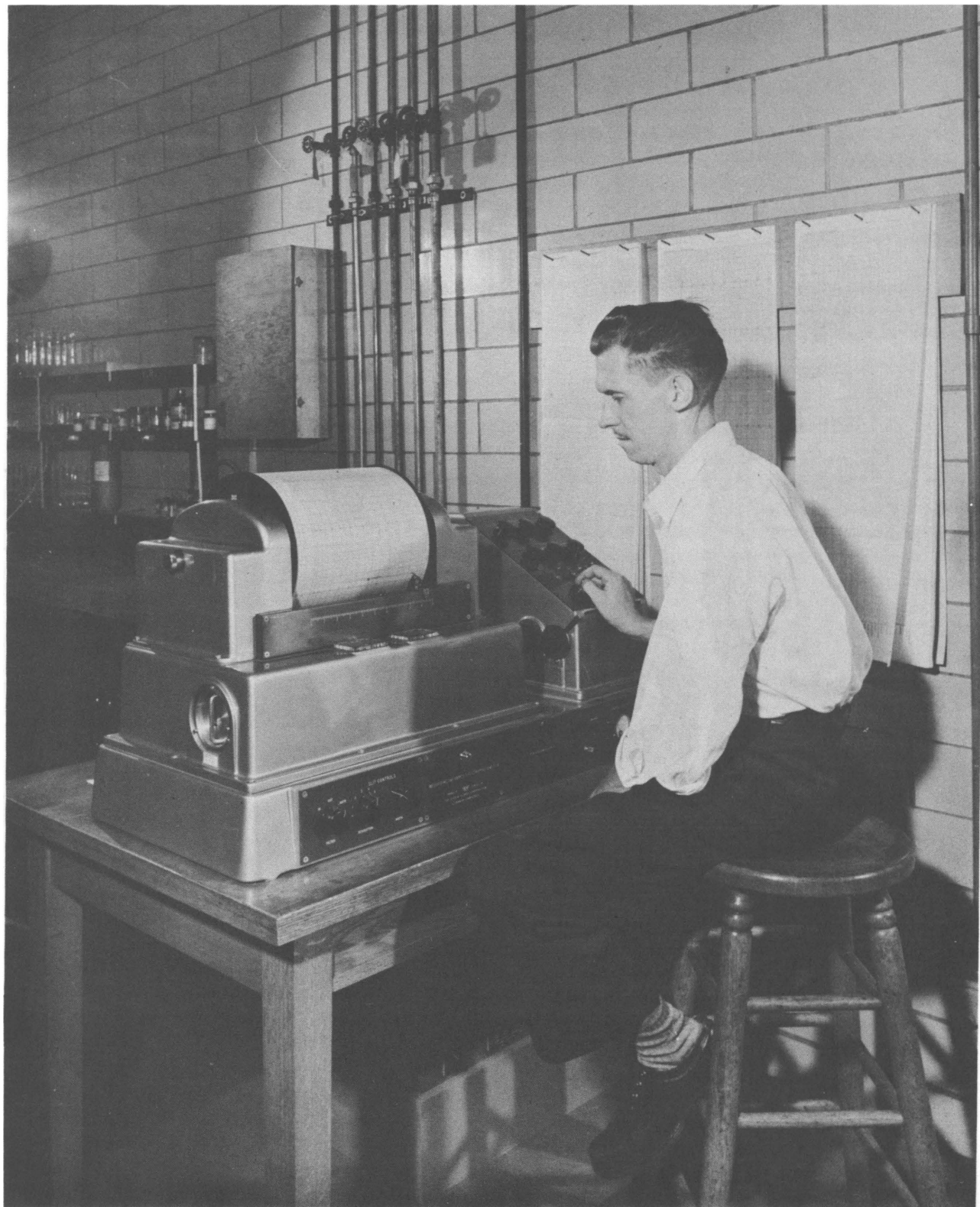


Figure 41. - Double-beam infrared spectrometer.

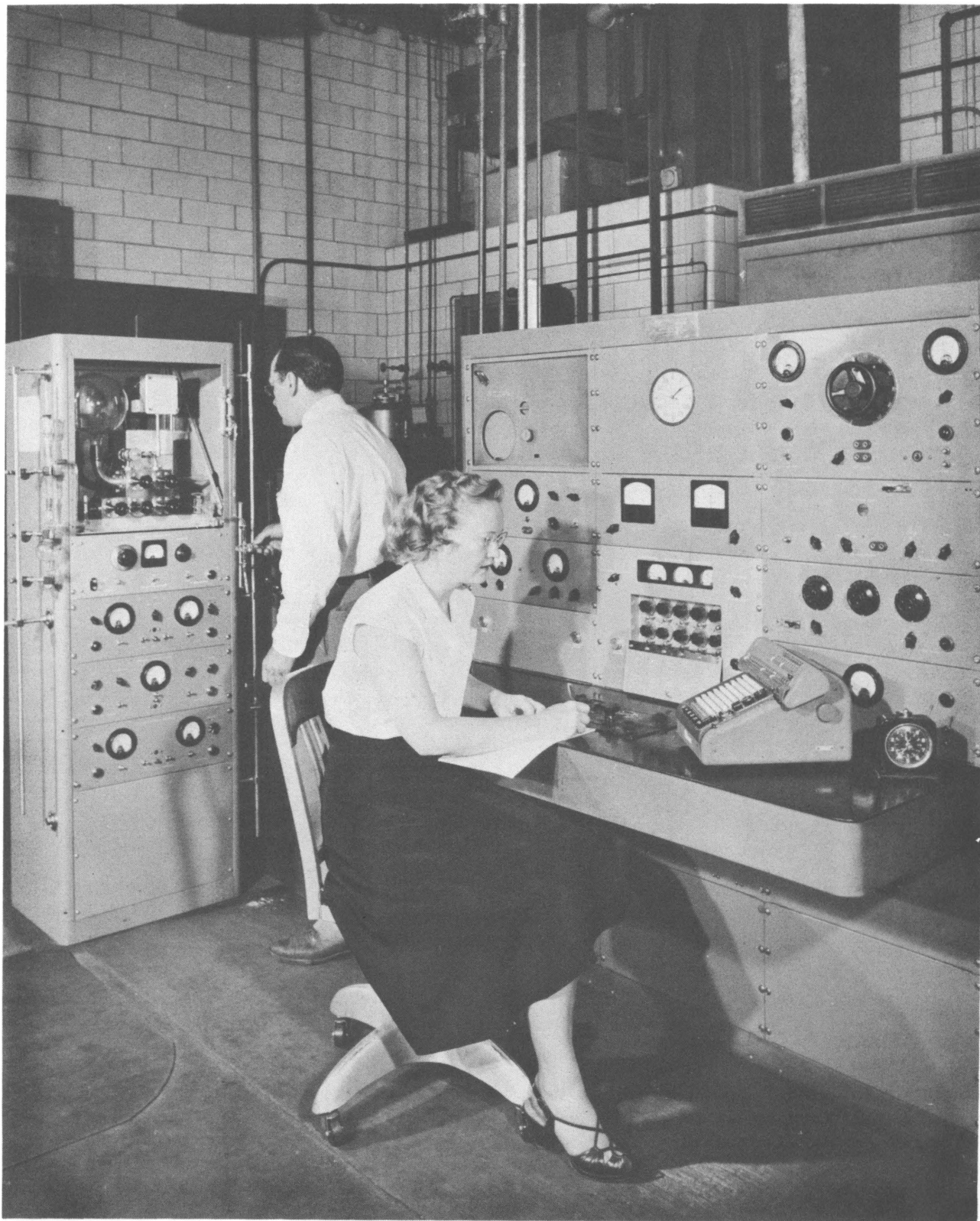


Figure 42. - Revised mass spectrometer.

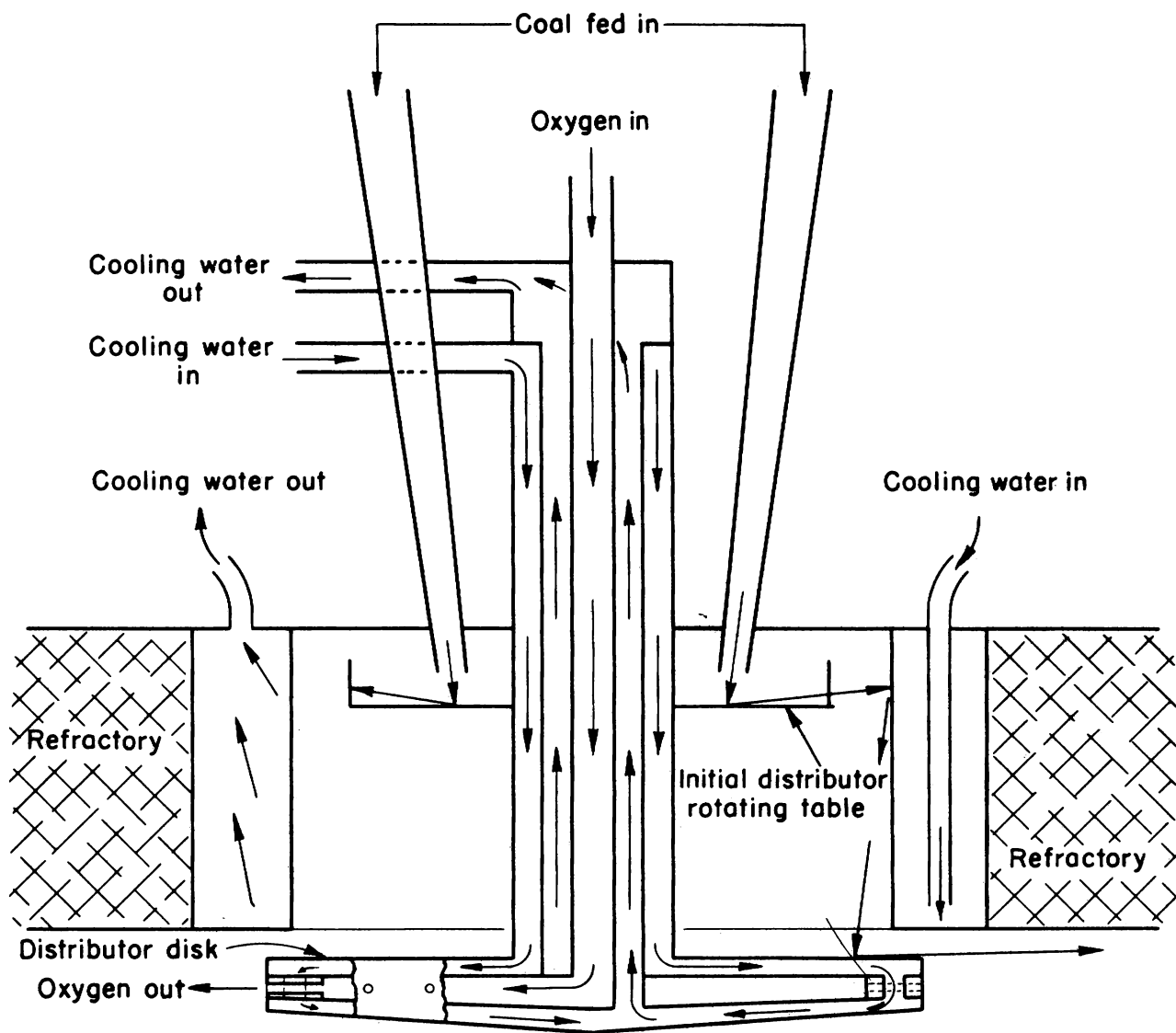


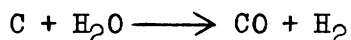
Figure 43. - Coal feeder for vortex gasifier.

A mass spectral method (fig. 42) has been developed for analyzing paraffin-naphthene fractions of gasoline obtained from coal hydrogenation. By this technique, cyclopentanes and cyclohexanes with single and with multiple alkyl side chains can be distinguished from each other and from paraffins. As yet, the method is not easily extended to C₉ and higher hydrocarbons because of the scarcity of reference compounds. However, appreciable concentrations of a C₉ (hydrindane) and a C₁₀ dicyclic compound (methylhydrindane, decalin, or a terpane) have been identified in vapor-phase gasoline. The results of this analysis are incorporated in tables 18 and 19 (see Composition of Gasoline Obtained from Coal).

Gasification of Coal in the Vortex Reactor

Gasification of pulverized coal with oxygen and steam may be used for the production of synthesis gas (carbon monoxide plus hydrogen) for the Fischer-Tropsch process or of hydrogen for the hydrogenation of coal. This process has been studied in a vortex reactor to gain an insight into the operating variables and the performance characteristics of such a system and as a means of predicting the optimum conditions for adiabatic gasification of coal. The construction of the reactor and the flow diagram of the unit have been shown in the 1949 Annual Report (Bureau of Mines Report of Investigations 4651); a diagrammatic sketch of the coal feeder (fig. 43) shows the path of the coal into the reactor, as well as the oxygen outlet that permitted introduction into the reaction zone of part of the oxygen with the coal. The vortex reactor had a diameter of 2 feet, and its depth was varied from 2 to 36 inches. The unit was preheated to 2,000° F. with a mixture of natural gas, air, steam, and oxygen. After the reaction temperature was reached, the gas and air were shut off, and coal was admitted at the rate of 100 pounds per hour. Oxygen and steam were preheated to 1,300° F. and added in such amounts that the oxygen:coal ratio ranged from 7 to 11 cubic feet per pound, while the ratio of steam to coal was maintained at 0.55 pound per pound.

By introducing some of the oxygen with the coal (instead of introducing all of it through the tangential slots of the reactor), the production of synthesis gas was increased considerably under otherwise equal conditions. Increasing the oxygen:coal ratio resulted in higher reaction temperatures. Because the unit was not an adiabatic reactor, more heat was lost at the higher temperatures by radiation and convection; such losses can be reduced substantially in larger installations. The gasification reaction,



did not begin until most of the oxygen had been consumed. Steam and oxygen also reacted with the volatile matter distilled from the coal; but the amount of carbon monoxide and hydrogen produced in this manner was small, so that residual char (after devolatilization of the coal) was the principal source of synthesis gas. The rate of gasification of coal was approximately of first order with respect to the amount of carbon available, at least up to space velocities of 33 pounds of coal per cubic foot of reactor space per hour. By changing the depth of the vortex reactor, the space velocity of the coal was

in effect varied without changing its rate of flow. Evaluation of the data, obtained over a range of radial and space velocities as well as reaction temperatures, showed that the rate of gasification was diffusion-controlled above about 2,200° F.

As the radial velocity at a given space velocity increases with the diameter of the vortex, higher conversion is attainable with reactors of larger diameter when diffusion is rate-controlling. For example, complete gasification of the available carbon appears to be possible at sufficiently high temperatures in an adiabatic vortex reactor of 8-foot diameter over a wide range of space velocities of coal. Using empirical rate data, methods were developed for predicting the performance of such adiabatic reactors, and a ratio of 7 to 7.5 cubic feet of oxygen per pound of coal appeared to be most economical for the production of synthesis gas. For this optimum ratio, 34.1 pounds of coal and 247 cubic feet (S.T.P.) of oxygen are needed to produce 1,000 cubic feet (S.T.P.) of carbon monoxide plus hydrogen.

Technical Publications

A book by Storch, Golumbic, and Anderson on the Fischer-Tropsch and Related Syntheses has been published by John Wiley & Sons, Inc., and contains an exhaustive and critical review of the large number of reports and documents pertaining to this subject. In addition, much information on thermodynamics and on heterogeneous catalysis is included.

A Bibliography of Pressure Hydrogenation (of coal) has been completed. Parts I and II, covering literature and patents, respectively, have appeared as Bureau of Mines Bulletin 485; part III, comprising the indexes, will be published in the near future. A two-part Bibliography of Fischer-Tropsch and Related Processes, containing about 6,000 annotated references, is being completed; the literature section is to be printed soon, and the patent review is being assembled and typed.

Reviews on the current status of fluid dynamics, of the oxo synthesis, and of Bureau of Mines work on synthetic liquid fuels have been presented in various journals, and translations of foreign documents concerning the Fischer-Tropsch synthesis have been made available as information circulars of the Bureau of Mines. About 1,000 copies of each issue of Synthetic Liquid Fuels Abstracts, a bimonthly publication, were sent to the mailing list. However, curtailed appropriations have compelled at least temporary suspension of this service.

RESEARCH AND DEVELOPMENT, SYNTHESIS-GAS LABORATORIES AND PILOT PLANTS,
MORGANTOWN, W. VA., AND FIELD TESTS, GORGAS, ALA.

Experimental Development of Processes for Producing Synthesis Gas

There is an ever-increasing appreciation of the fact that the new developments in coal gasification are of major importance in determining the cost of synthetic liquid fuels. The cost of synthesis gas is 60 to 70 percent of the total cost of gasoline produced from coal by the gas synthesis process. Intensive work has been conducted on the experimental development of pulverized coal gasification with oxygen and steam at Morgantown, W. Va. Field-scale experimentation in underground gasification of coal has continued at Gorgas, Ala.

During the past year planning of improved facilities for process development work in coal gasification was continued in connection with the new Bureau station at Morgantown that has been approved by Congress.

Pulverized-Coal-Gasification Pilot Plants,
Morgantown, W. Va.

During the past year experiments have been carried on in three types of gasification units. The results of work on the smallest unit are contained in a report^{1/} recently issued. In this unit about 50 pounds of powdered coal is gasified per hour, and its operation has resulted in a better understanding of the conditions under which a given coal can be gasified with maximum efficiency.^{2/} This apparatus proved to be convenient also for evaluating the ease with which various types of coal can be gasified.

Atmospheric Pressure Gasifier

The large (500 lb. coal/hour) atmospheric pressure generator, previously described^{3/4/} was remodeled to reduce the interior diameter so that, with the auxiliary equipment available, runs could be made more nearly at capacity. During the year eight more test runs were made in this unit, which then was dismantled to make room for a newly designed atmospheric-pressure gasifier.

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- ^{1/} Sebastian, J. J. S., Edeburn, P. W., Bonar, F., Bonifield, L. W., and Schmidt, L. D., Laboratory-Scale Work on Synthesis-Gas Production: Bureau of Mines Rept. of Investigations 4742, 1951, 41 pp.
 - ^{2/} Sebastian, John J. S., Effect of Variables in Powdered Coal Gasification: Presented before the Gas and Fuel Division of the American Chemical Society, Diamond Jubilee Meeting, New York, N. Y., Sept. 7, 1951.
 - ^{3/} Synthetic Liquid Fuels Annual Report of the Secretary of the Interior for 1950, Part I. - Oil from Coal: Bureau of Mines Rept. of Investigations 4770, 1951, pp. 51-58.
 - ^{4/} Strimbeck, G. R., Holden, J. H., Rockenbach, L. P., Cordiner, J. B., Jr., and Schmidt, L. D., Pilot-Plant Gasification of Pulverized Coal with Oxygen and Highly Superheated Steam: Bureau of Mines Rept. of Investigations 4733, 1950, 41 pp.

This new unit gasifies about 500 pounds of coal per hour. It was designed in cooperation with the Babcock & Wilcox Co., which also fabricated the unit. This gasifier, shown in figure 44, was designed to determine the physical construction that would be necessary in a larger-scale apparatus; that is, it can be considered the prototype of a large-scale gasifier. Studies will be made of (1) slag tapping and (2) the behavior of slag on water-cooled tubes, which can be installed to simulate a waste-heat boiler. The unit is constructed so that individual sections (that is, the slag pot, primary reaction zone, secondary reaction zone, and gas-cooling zone) may be changed or revised without changing other sections. The reactants, coal and oxygen at atmospheric temperature and steam at 1,000° F., are introduced at the top of the primary reaction zone. The two coal and oxygen nozzles are directed downward in such a way as to impinge on the pool of liquid slag at the bottom of the gasifier and, at the same time, impart a spin to the reactants in the gasifier. Ample provision also has been made for introducing reactants at other locations in the reactor.

A small portion of the make gas is drawn down through the lower throat into the slag pot and thence back to the main gas stream to help in attaining adequate throat temperatures for slag tapping. The larger portion of the make gas goes upward into the secondary zone; the purpose of this zone is to provide cooling, so that the fly ash carried in the gas will not coat the cooling tubes. From the cooling zone the gas goes to the dust-removal train. The latter is substantially as described in Report of Investigations 4733,^{5/} except that the cyclone dust collectors have been removed. Experience indicates that the residues removed in the dust train are high in ash content and consequently have so little value that dry removal is unnecessary. In figure 45 the lower part of the unit, slag pot, and part of the primary reaction zone are shown. Figure 46 is a view of the upper part of the unit. Test runs on this gasifier were begun in August 1951 and are continuing. Too few data have been obtained to permit drawing final conclusions. However, the unit has functioned well mechanically, and it has been shown that the gases can be handled in the cooling section without serious build-up of fly ash on the tubes. The present work is concentrated on reactant-nozzle design and placement.

Pressure Gasifier

Synthesis gas is almost always used at high pressures. The cost of compressing synthesis gas to the pressure at which it is used is a major cost item. Consequently, it is desirable to develop a gasifier that will operate at pressures somewhat above that of the usage pressure. In the case of Fischer-Tropsch plants for making synthetic liquid fuels, this usage pressure is about 30 atmospheres or approximately 450 p.s.i. The experimental pressure gasifier built at Morgantown is designed for gasifying 500 pounds of powdered coal per hour at an operating pressure of up to 30 atmospheres.^{6/} Figures 47 and 48 show the design of this pressure gasifier. Early test runs in this high-pressure unit have been made at 100 p.s.i. pressure, using oxygen at atmospheric temperatures and steam at 1,000° F. Because of difficulty in obtaining proper equipment, the oxygen has not been preheated. New equipment now on order will permit work at high oxygen temperatures and higher gasifier pressures.

^{5/} See footnote 4.

^{6/} See footnote 3.

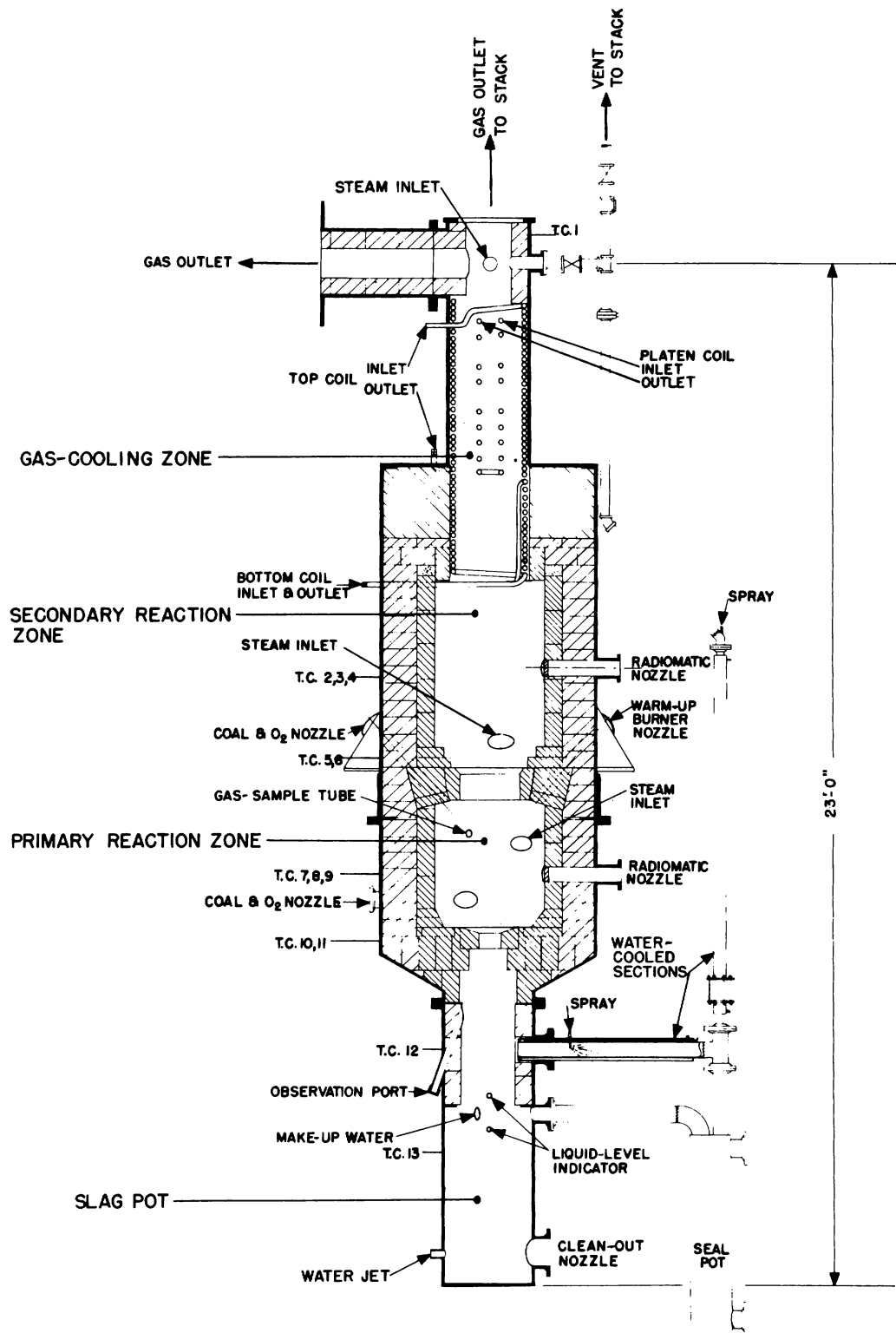


Figure 44. - Atmospheric generator design 4.

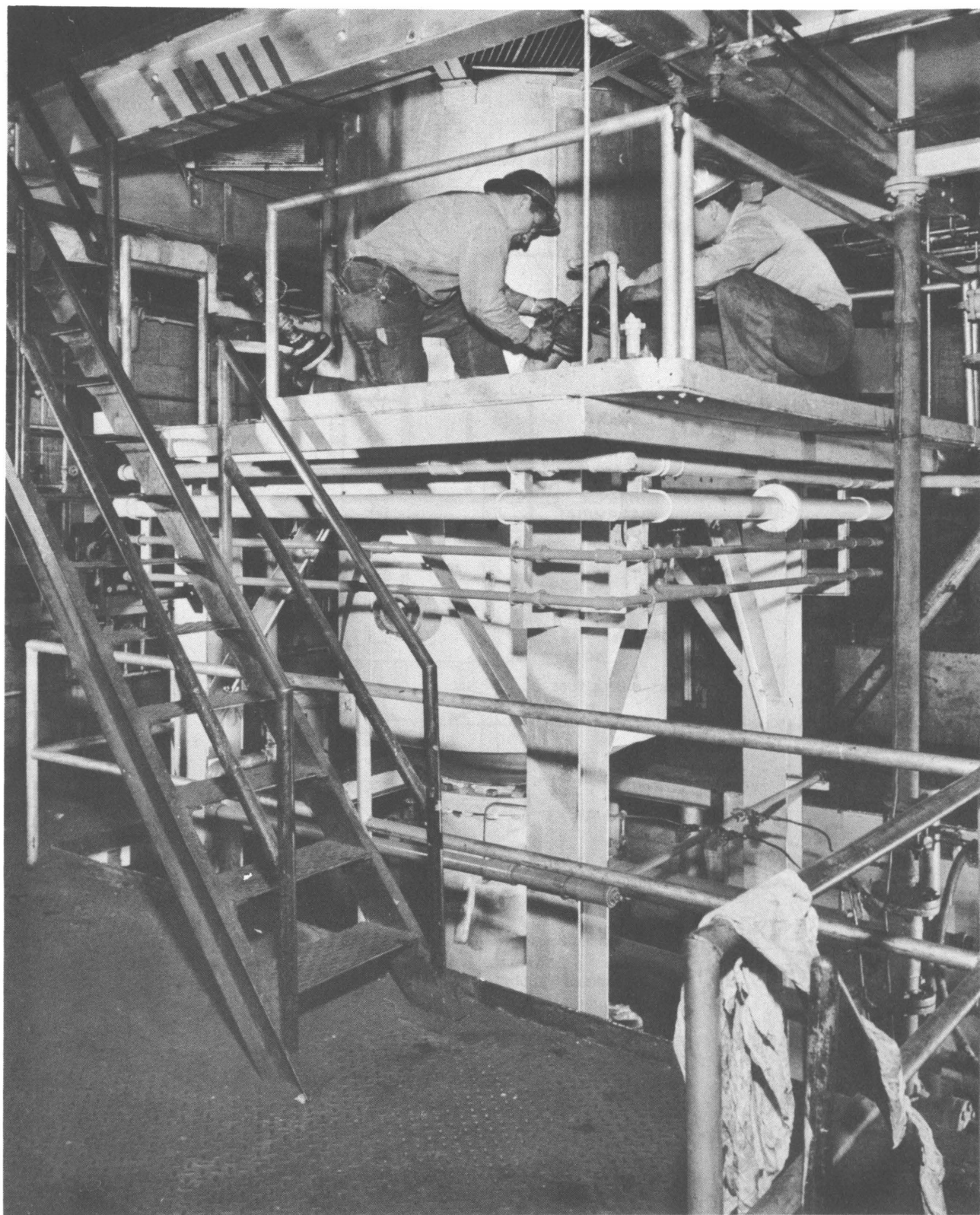


Figure 45. - Atmospheric-pressure gasifier (capacity, 500 pounds of coal per hour), showing slag pot and primary and secondary reaction zones.

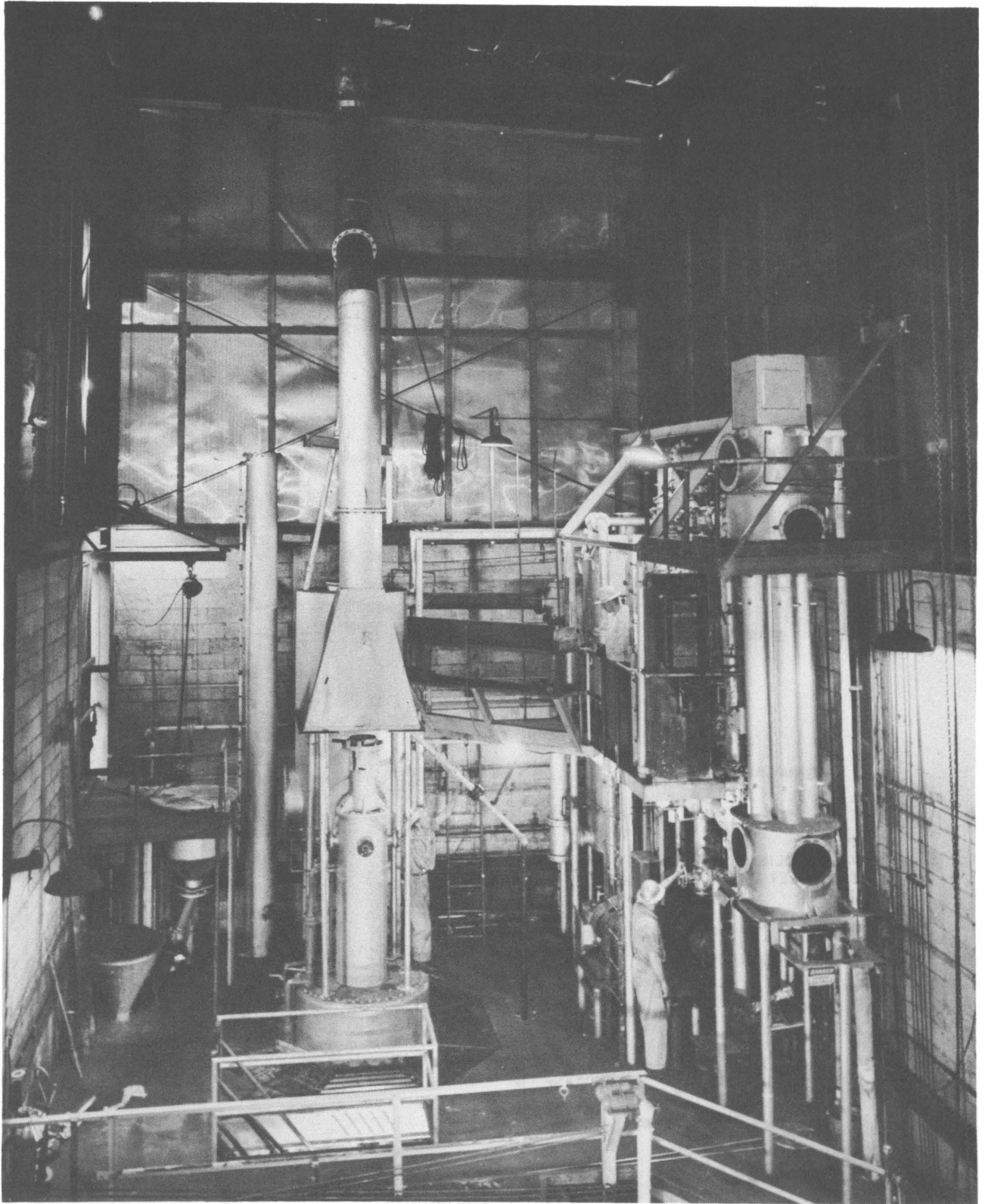


Figure 46. - Atmospheric-pressure gasifier (capacity, 500 pounds of coal per hour), showing upper part of unit and dust-removal equipment.

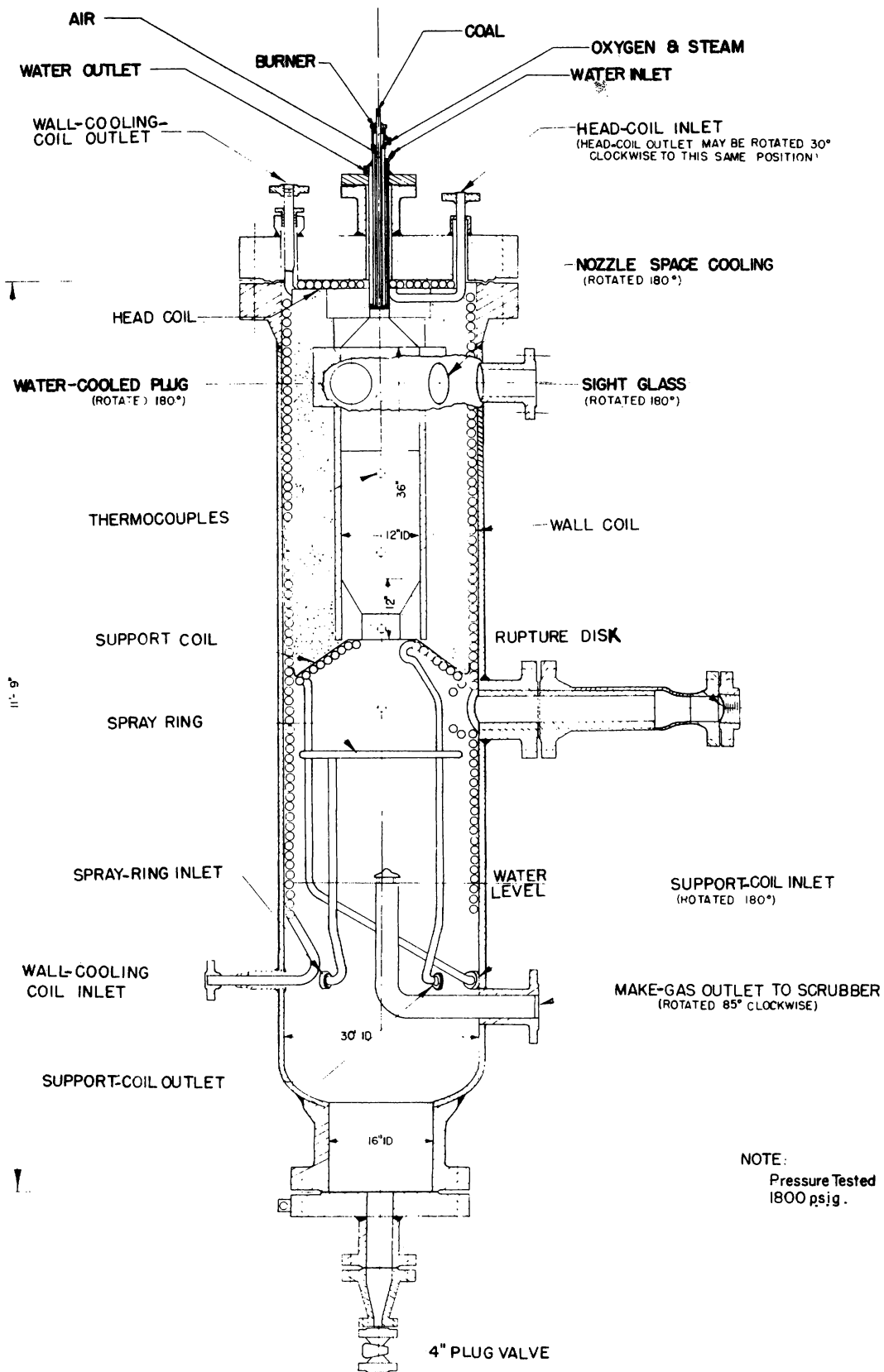


Figure 47. - Reactor for pressure gasification.

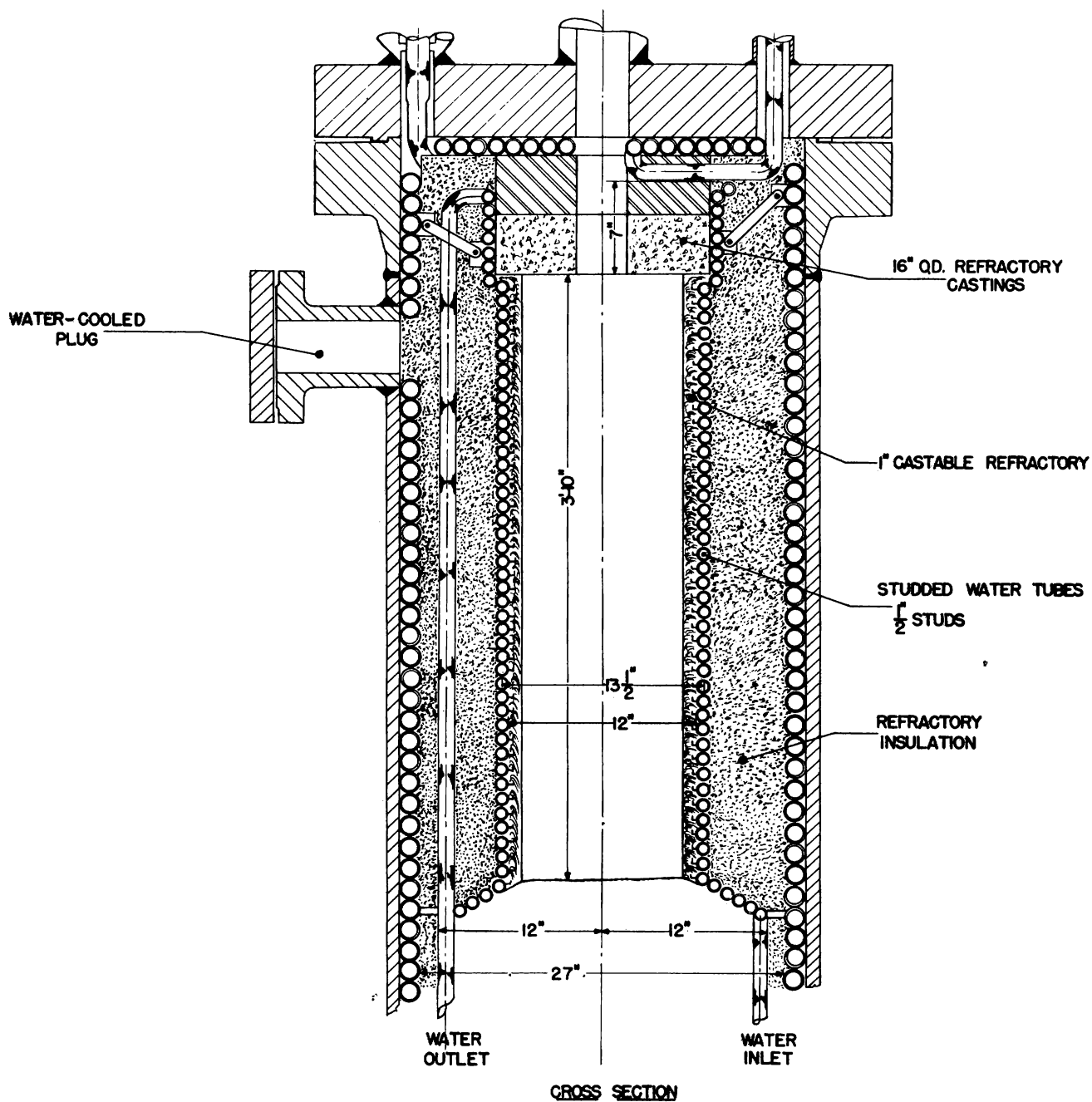


Figure 48. - Pressure gasifier refractory and water walls (upper section).

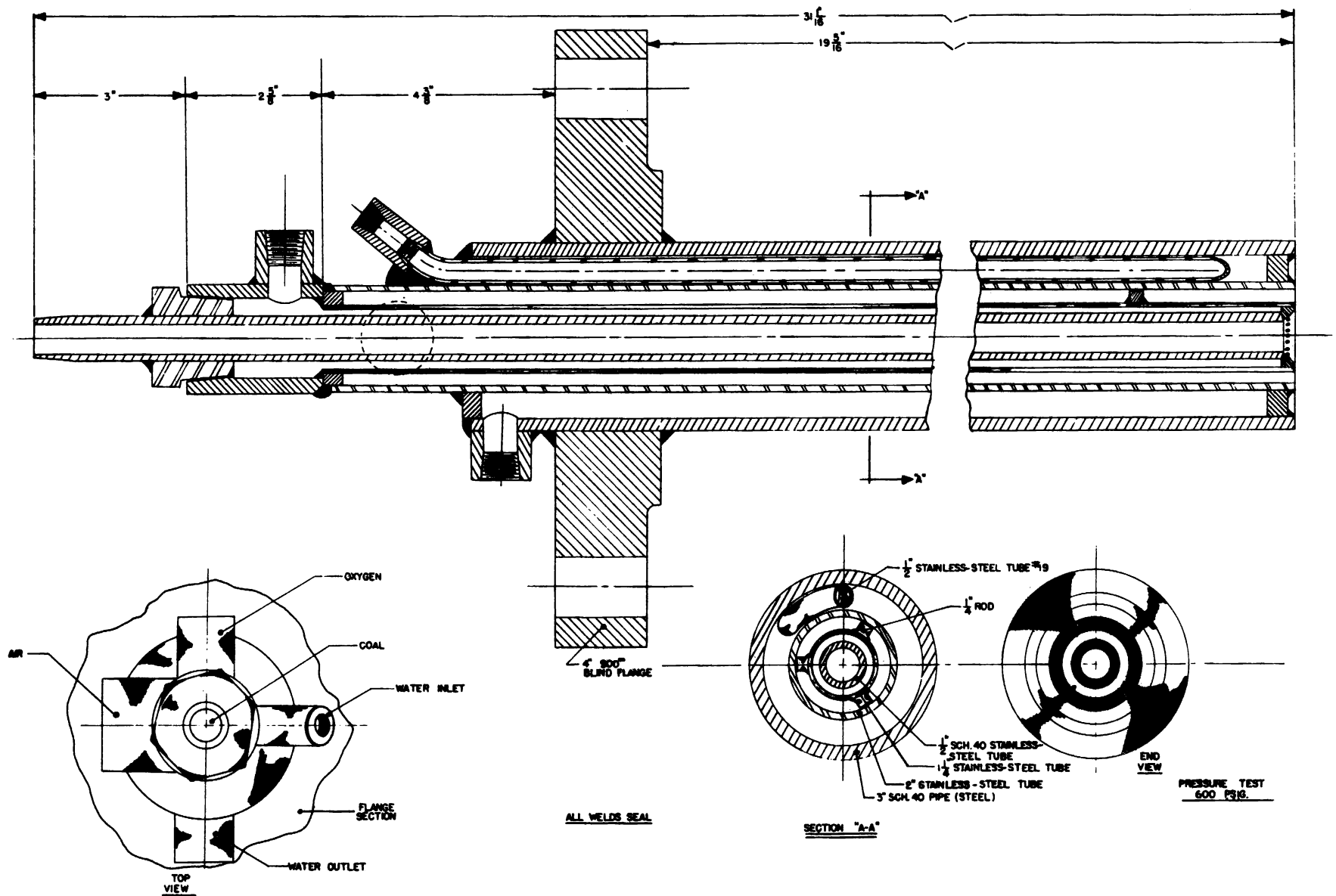


Figure 49. - Combination heat-up and reactant injection nozzle.

In the early runs, the reactants were introduced through separate nozzles. These nozzles were in a horizontal plane and tangent to about a 4-inch-diameter circle. Early tests showed that refractory linings could not be maintained in the upper part of the generator under these conditions. A new nozzle (fig. 49) was designed to introduce all reactants vertically downward through the top. The coal - carried by inert gas - enters through the center tube. Into the space around this tube the oxygen and steam are introduced the mixture is injected into the coal stream through the small holes. This method of entry results in excellent mixing of the reactants and prevents development of excessive heat at the top of the generator. This nozzle is also used as a heat-up burner. For that purpose, natural gas is admitted through the coal tube, oxygen through the next concentric space, and air through the next space. During a run, a small amount of inert gas is admitted to the air space. This provides some insulating effect between the jacket and the oxygen-steam tube. Test runs with this nozzle have shown very high percentages of gasification at low oxygen consumption and with little refractory damage.

The original generator design provided for a support coil to carry the refractory lining. Tests showed that the cooling effect from this coil was excessive at the slag throat. Several turns have been removed from the coil, and the gasifier internal diameter of the refractory lining is now 12 inches along its entire length.

Throughputs of more than 115 pounds of coal per cubic foot of reactor volume per hour have been obtained at 100 p.s.i.g. These high throughputs were even greater than anticipated and promise lower gasification costs than expected. Table 20 shows the performance of the pressure gasifier at this high throughput rate. The high percentage of carbon gasified, together with the rather low requirements of coal, oxygen, and steam per thousand cubic feet of hydrogen and carbon monoxide produced, also promise lower costs. Performance in a large-scale gasifier no doubt would be still better because of decreased heat loss per pound of coal gasified. Severe erosion of the refractory lining occurred during the tests. Additional tests will be made to determine whether operation with a water-cooled coil covered with a "steady-state" thickness of slag is feasible.

The projected program for this unit calls for test runs in the pressure range 100 to 450 p.s.i.g., using superheated steam, preheated oxygen, and preheated coal.

All of the pilot-plant work has demonstrated that pulverized coal can be satisfactorily gasified under ash-slagging conditions, with economical consumption of oxygen. The program as now projected calls for intensive testing and equipment development for both high- and low-pressure gasification.

TABLE 20. - Typical performance of pressure gasifier operating at 100 pounds per square inch pressure on pulverized, Sewickley-bed coal

Duration of run.....	hours	10
Raw coal rate.....	lb./hr.	463
Steam inlet temperature.....	°F.	931
Process oxygen inlet temperature.....	do.	60
Coal inlet temperature.....	do.	327
Oxygen input per pound coal.....	std.cu.ft.	9.2
Steam input per pound coal.....	lb.	0.3
Synthesis gas analysis (corrected for inert gas introduced with coal) percent:		
CO ₂		7.1
Illuminants.....		.5
H ₂		34.4
CO.....		55.4
CH ₄4
H ₂ + CO.....	std.cu.ft. per hour	12,870
Total carbon gasified.....	percent	88
Coal required per M.c.f. (H ₂ + CO).....	lb.	36
Oxygen required per M.c.f. (H ₂ + CO).....	std.cu.ft.	333
Process steam input per M.c.f. (H ₂ + CO).....	lb.	10.9

Auxiliary Experiments

Some small-scale experiments have been carried out on a gasifier that uses pulsating flow. The objective of pulsating flow is to increase the rate of transferring both heat and material to the carbon particles by moving the gas surrounding the particle back and forth past the particle so that the carbon continually comes in contact with more gasifying agent. The pulsations are achieved by providing a gasifier with an exit too small to carry off immediately all the products of reaction. The resulting pressure rise causes a momentary stop in the reactant supply, in turn causing the pressure to fall. The resulting pressure fluctuations cause waves to travel down the exit pipe, moving the gas with respect to the carbon particle. Insufficient data are available to draw firm conclusions as to the operating characteristics of this gasifier, but pulsations have been achieved at about 100 cycles per second, and throughput rates of the order of 1,000 pound of coal per cubic foot of gasifier volume per hour have been obtained. No data are available on the percentage gasification of the coal at these high throughput rates. Severe erosion of the refractory lining occurred, and the possibility of operation with a slag-covered, water-cooled reactor wall is to be investigated.

Since the gasification of powdered coal is, in general, a cocurrent process, the exit gas leaves at a high temperature, carrying with it a considerable amount of sensible heat. To utilize this sensible heat, it must be transferred to the entering reactant streams. Hence, studies have been carried out on preheating of the entering coal. Powdered coal in dense phase flow from the feeder (described in the two previous Annual Reports) is passed through a tube in the form of a coil that is heated externally. Coal side-heat transfer coefficients

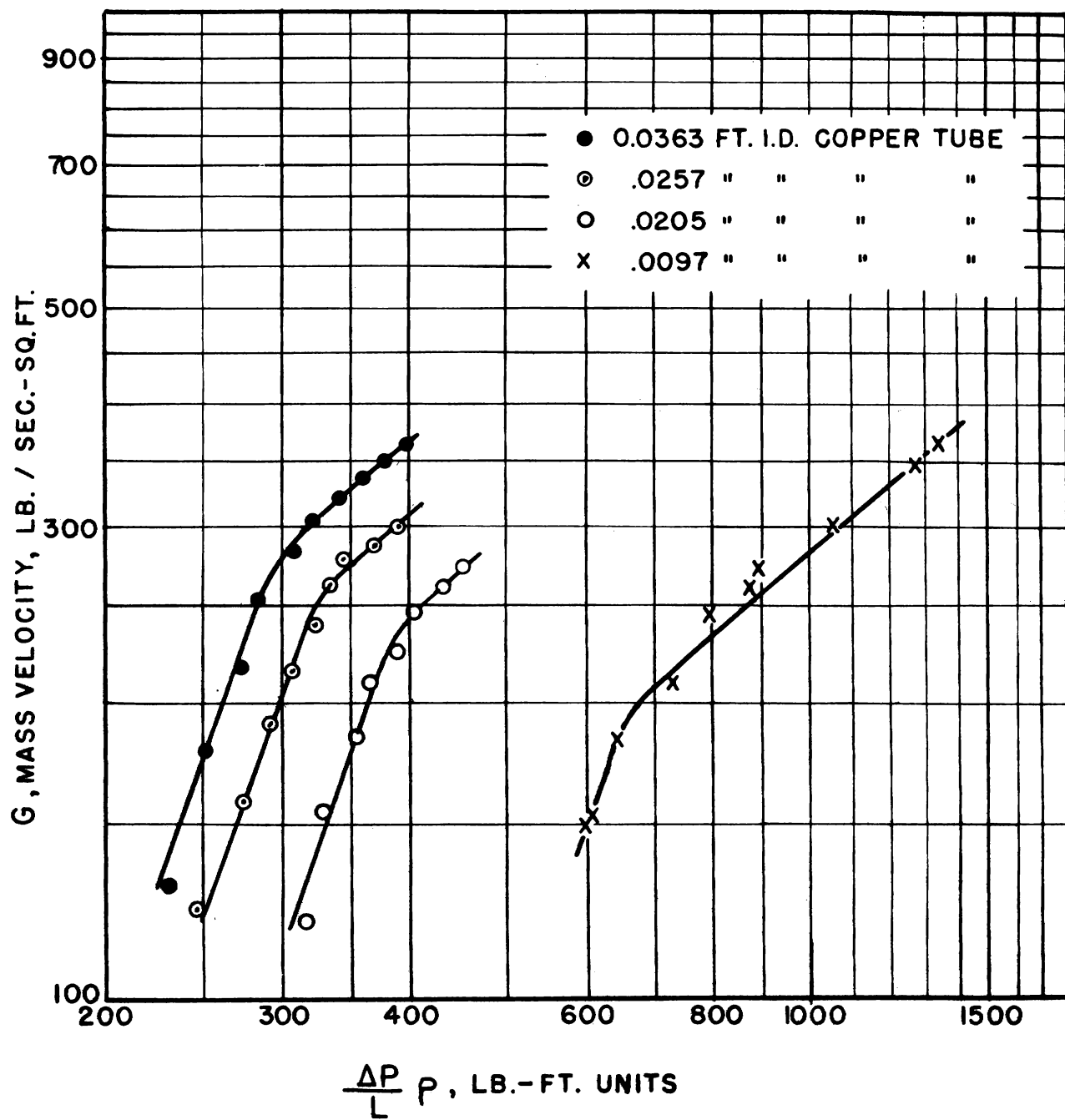


Figure 50. - Effects of $(\Delta p/L)\rho$ on resulting mass velocity in various sizes of tubes.

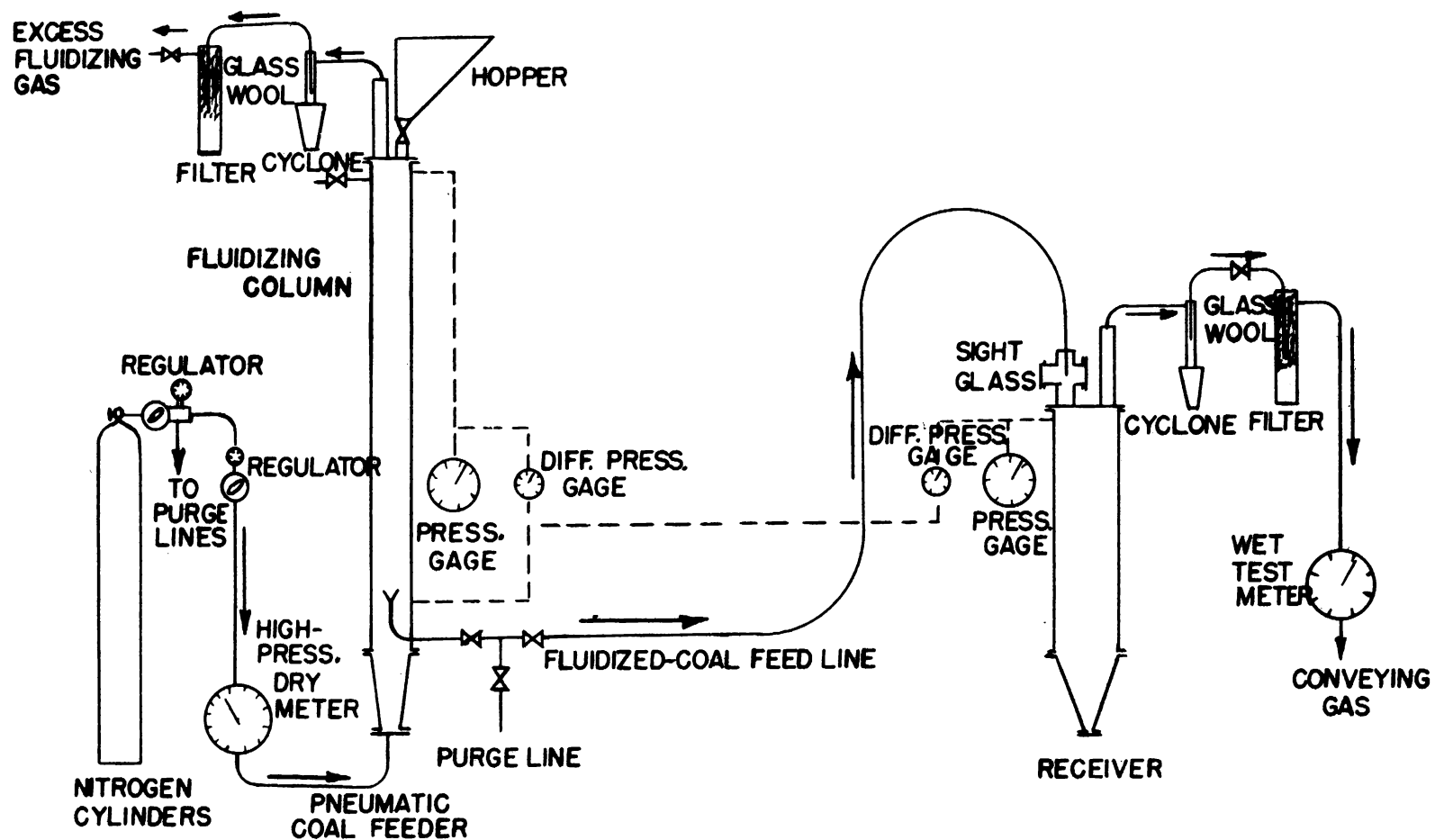


Figure 51. - Apparatus for study of continuously feeding finely powdered coal at superatmospheric pressures.

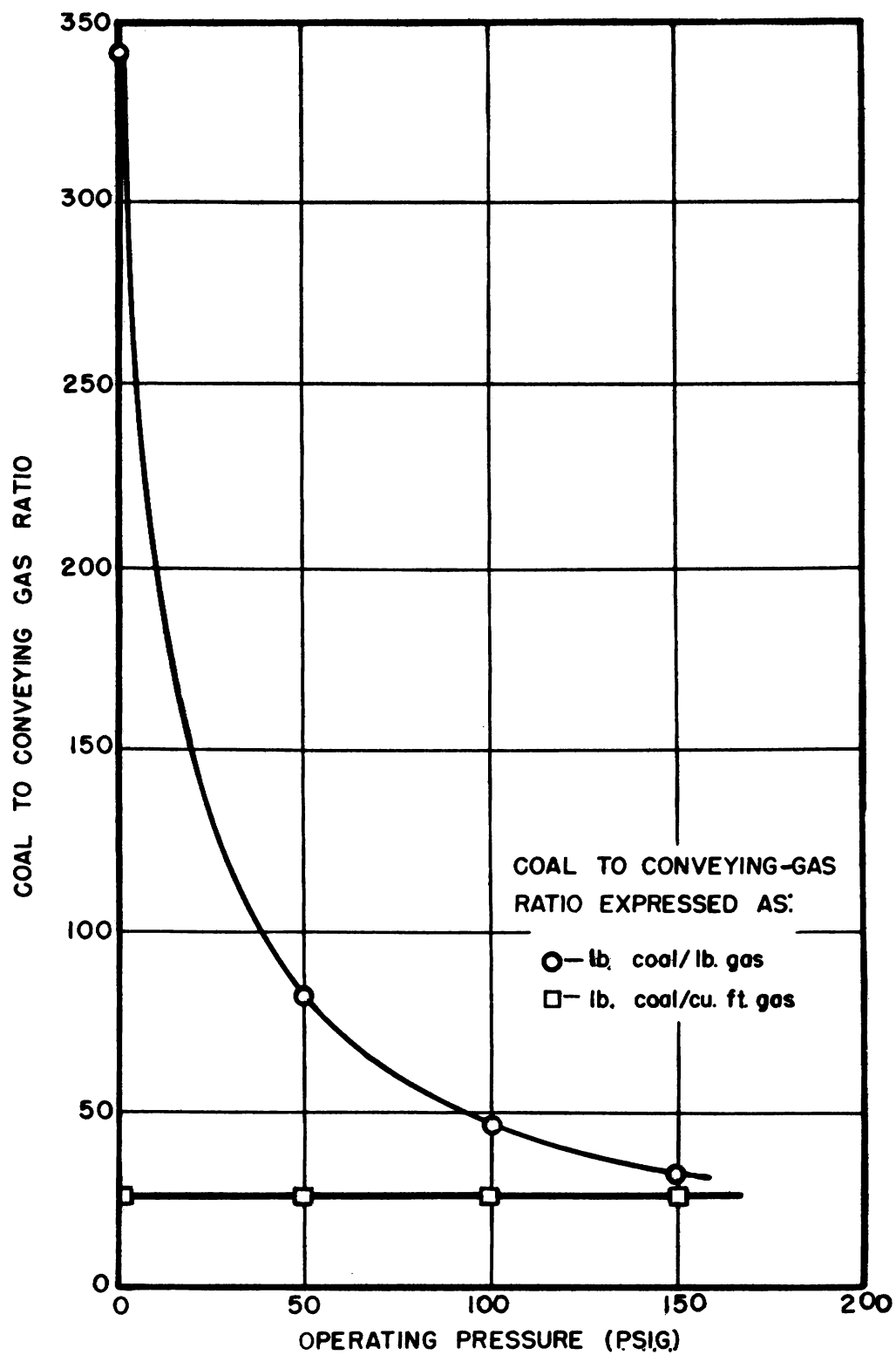


Figure 52. - Effect of operating pressure on coal:conveying-gas ratio.

of the order of 40 B.t.u. per square foot per hour per degree F. have been determined. It has been demonstrated that coking coal can be heated to 700° F. in a small-diameter tube (0.2 inch inside diameter) without build-up of any deposits on the tube wall. The use of preheated coal as feed to a gasification unit will be tested on the small gasifier during the coming year.

Pressure drop measurements on the flow of dense coal-air mixtures through tubes^{7/} have been correlated on an empirical basis. Figure 50 shows $(\Delta p/L) \rho$ plotted against the mass velocity, where $\Delta p/L$ is the pressure drop in pounds per square foot of length and ρ is the average density of the coal-air mixture in pounds per cubic foot. The curves may be considered to consist of two straight segments. Because the points of inflection lie on a straight line and the lines for the different diameters are parallel, an empirical equation that represents the results with an accuracy of about 5 percent is given below.

$$\text{For } G(\Delta p \rho / L)^{0.35} > 1950, \quad \Delta p \rho / L = 0.022 G^{1.12} / D^{0.94}$$

$$\text{and for } G(\Delta p \rho / L)^{0.35} < 1950, \quad \Delta p \rho / L = 3.5 G^{0.35} / D^{0.73}.$$

G is the mass velocity in pounds per second per square foot, and D is the inside diameter of the tube in feet.

Conveying and Feeding Powdered Coal Under Pressure

As the high cost of compressing synthesis gas favors gasifying coal at elevated pressures, it was necessary to develop a method for continuously conveying and charging finely powdered coal into a pressurized gas generator. Experimental work at pressures up to 150 pounds per square inch has been carried out in the apparatus shown in figure 51.

The investigations^{8/} showed that powdered coal can be conveyed pneumatically, in a dense phase, from a fluidized bed and discharged at a constant rate. With other conditions equal, the discharge rate was found to be solely a function of the pressure differential across a conveying line of given dimensions, irrespective of the magnitude of the operating pressure. As the difference in pressure between the fluidizer and receiver is increased, the coal feed rate increases. The amount of coal conveyed per unit volume of gas, measured at the existing pressure, is virtually constant at all operating pressures, as seen from the diagram in figure 52. For the type (high-volatile West Virginia bituminous) and particle size (83.5 percent through 200-mesh) coal conveyed by nitrogen through copper tubing (12 feet long, 3/16-inch inside diameter), and the type of upright funnel inlet used, this ratio was 25.7 pounds per cubic foot of conveying gas. However, the weight of coal carried per unit weight of conveying gas, represented by the upper curve, is seen to decrease rapidly with increasing operating pressures.

^{7/} Albright, C. W., Holden, J. H., Simons, H. P., and Schmidt, L. D., Pressure Drop in Flow of Dense Coal-Air Mixtures: Ind. Eng. Chem., vol. 43, 1951, pp. 1837-1840.

^{8/} Barker, K. R., Sebastian, J. J. S., Schmidt, L. D., and Simons, H. P., Pressure Feeder for Powdered Coal or Other Finely Divided Solids: Ind. Eng. Chem., vol. 43, May 1951, pp. 1204-1209.

Gas Purification

Development of Analytical Methods

During 1951, satisfactory procedures were established for determining nitric oxide, naphthalene, iron carbonyl, and solid and liquid impurities in crude and also in highly purified synthesis gas.

In connection with laboratory experiments on the catalytic removal of oxygen from synthesis gas, an analytical method was studied for determining low concentrations of oxygen in gas. The method adopted was a colorimetric one, which is described in the literature, but this laboratory increased the accuracy of the method by measuring the color intensity with a spectrophotometer rather than by visual comparison using Nessler tubes. The sensitivity of the method can be noted from the calibration curve shown in figure 53.

Bench-Scale Experiments

Bench-scale experiments were conducted to study the performance of a copper-chromium-vanadium catalyst at elevated temperatures and pressures for removing simultaneously the hydrogen sulfide and organic sulfur compounds from synthesis gas. Earlier work with this catalyst at atmospheric pressure has been described in the Annual Report for 1950. The pressure at which the operation is carried out has a considerable effect, both in the efficiency of sulfur removal and in the total amount of sulfur absorbed before regeneration is necessary. Employing two catalyst beds in series, operating at a pressure of 300 p.s.i.g. and temperatures of 450° and 300° C., the total sulfur content of raw synthesis gas containing 540 grains of H₂S and 33 grains of organic sulfur per 100 cu. ft. was reduced to less than 0.1 grain per 100 cu. ft. Indeed, the total sulfur outlet generally ranged from 0.00 to 0.02 grain per 100 cu. ft. Before regeneration was required, the catalyst absorbed about 15 percent of its weight in sulfur - about 40 percent more than at atmospheric pressure.

Figure 54 shows the bench-scale apparatus used in catalytic removal of sulfur at elevated pressures. Construction is underway on three catalyst reactors for use in the purification pilot plant.

At the request of the Demonstration Plant, a limited number of experiments were made to study the catalytic removal of small amounts of oxygen from synthesis gas. The tests were made at 575° F. and 300 p.s.i.g., using copper turnings as the catalyst. Employing space velocities as high as 20,000 standard cubic feet per cubic foot of reactor volume per hour, the oxygen content of the gas was reduced from 0.9 percent to less than 0.1 percent. In view of the fact that in plant practice the copper catalyst would be subjected to traces of sulfur, experiments were performed to study the catalytic activity of heavily sulfided copper. Results indicated that sulfided copper effects the removal of oxygen as efficiently as unsulfided copper. This catalytic activity of copper sulfide is important, as it eliminates the need of regenerating the copper catalyst when it becomes fouled with sulfur.

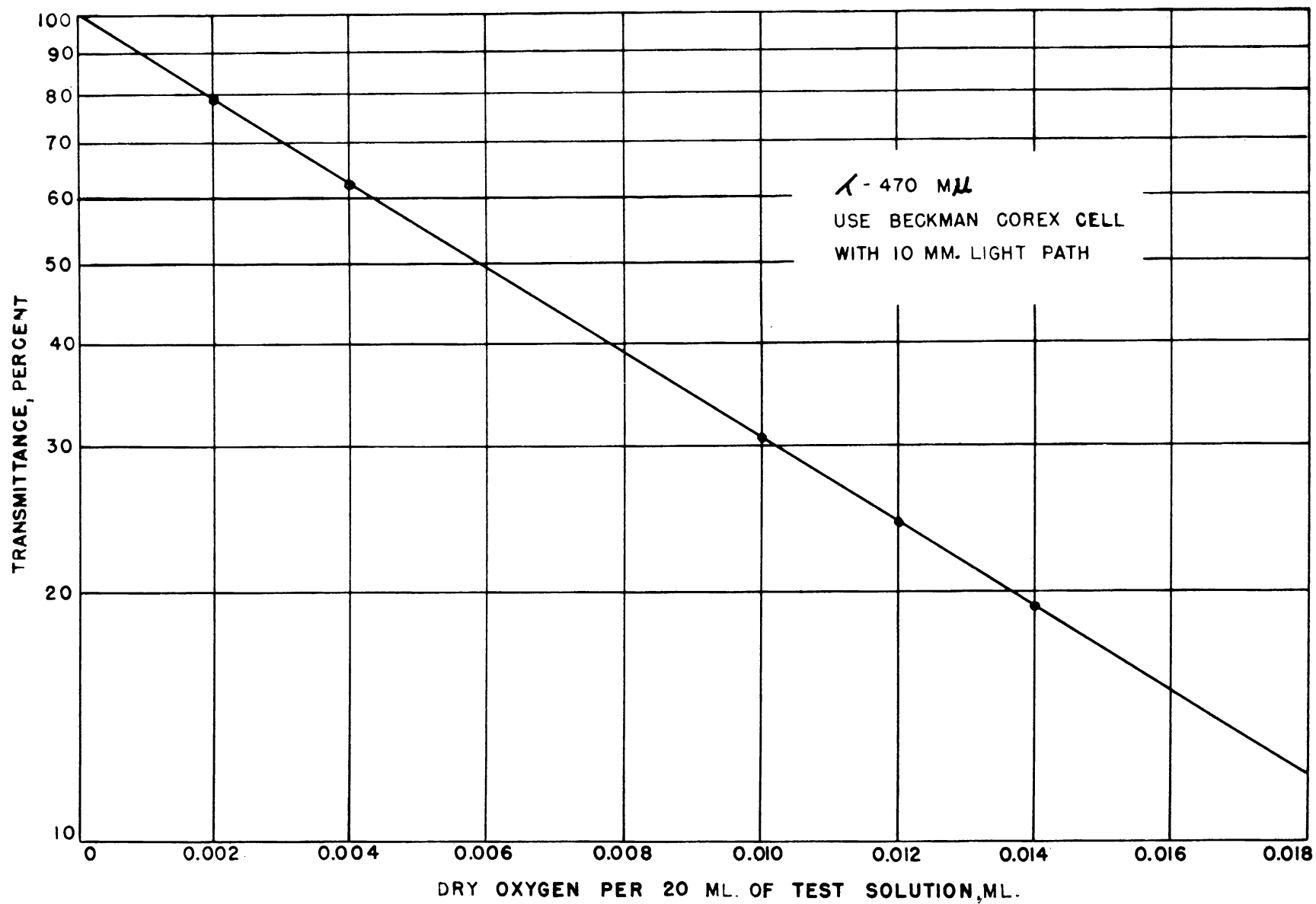


Figure 53. - Calibration curve for determining oxygen in gas.

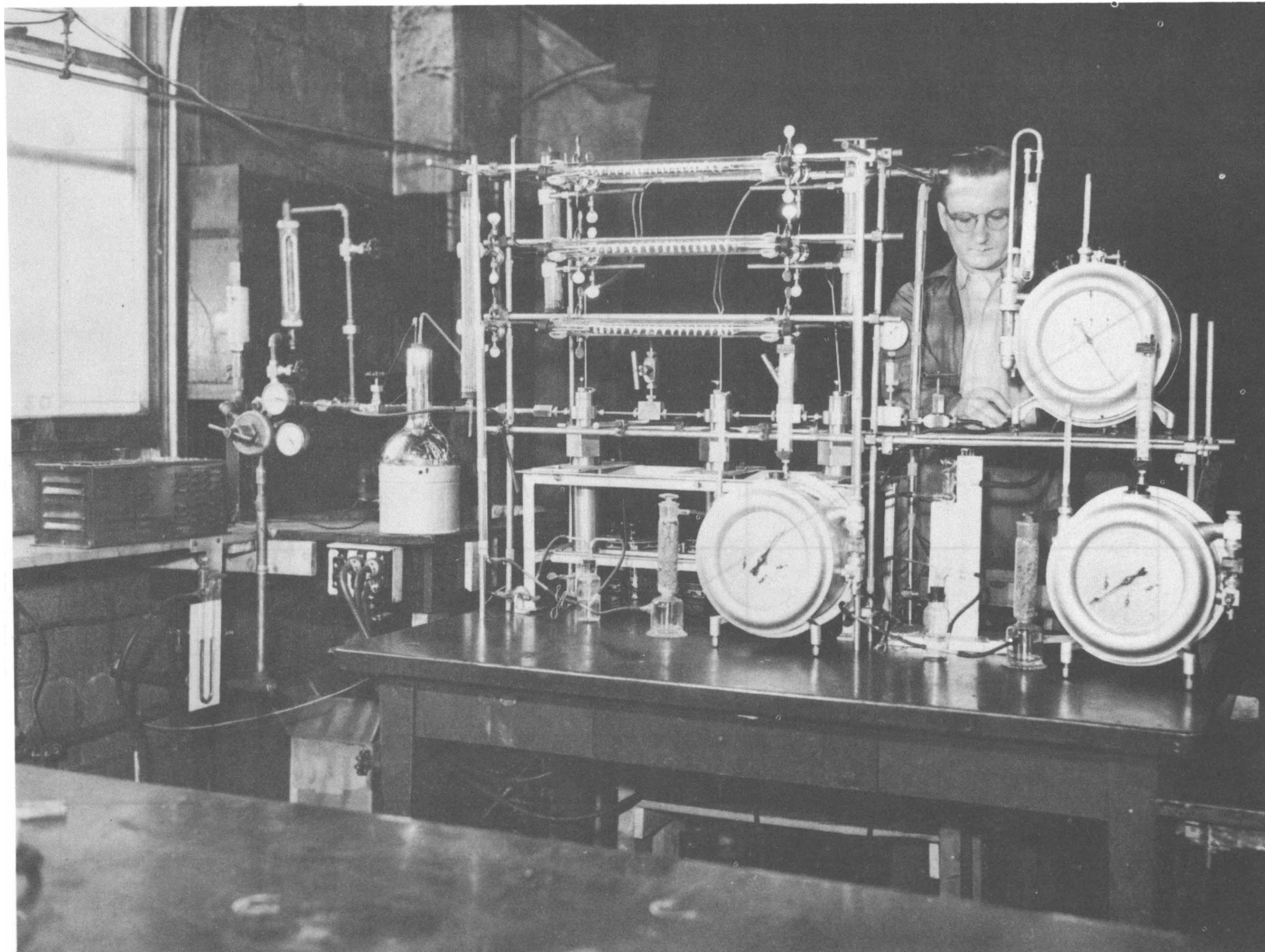


Figure 54. - Apparatus for removing hydrogen sulfide and organic sulfur compounds at elevated temperatures and pressures.

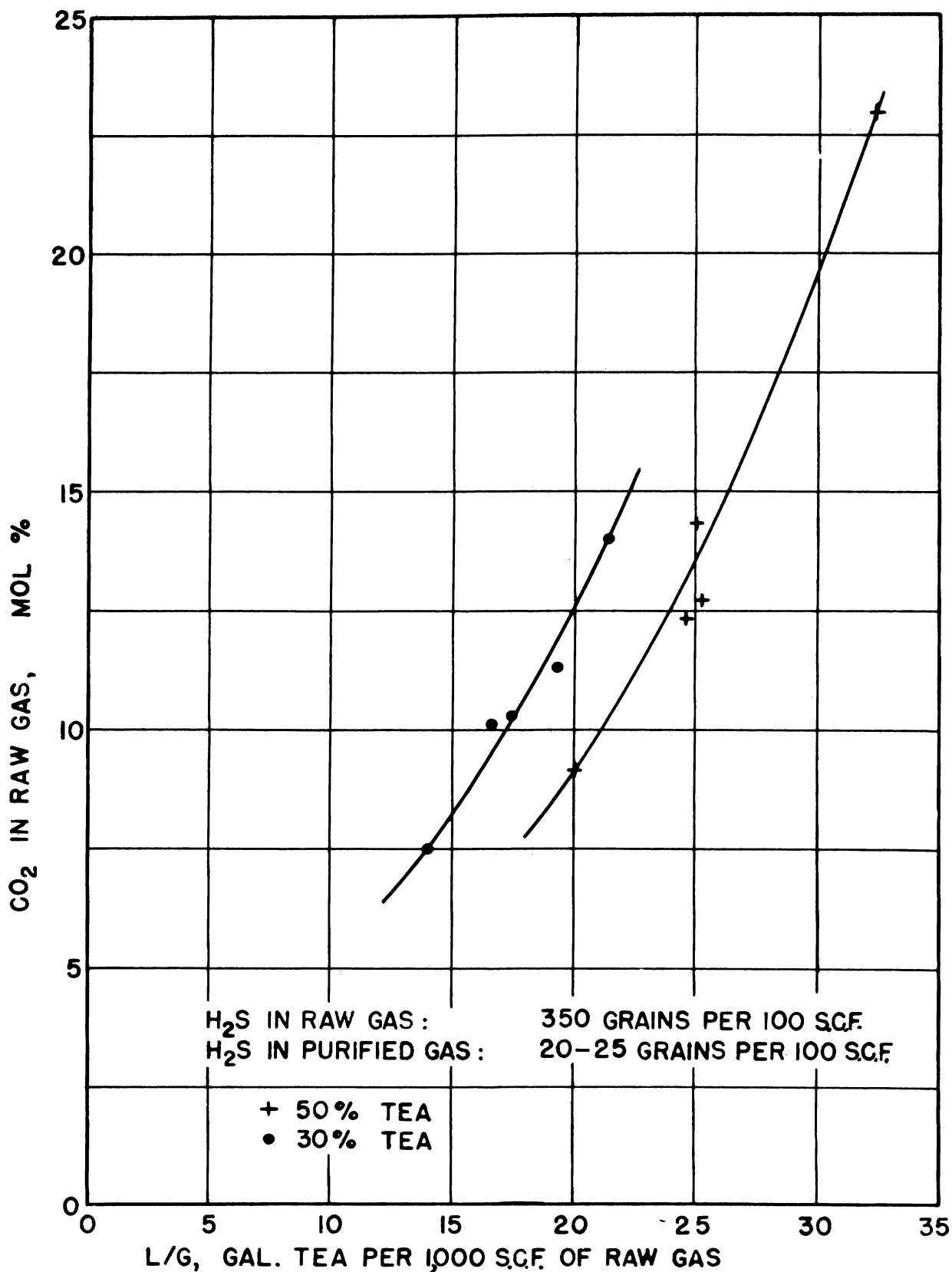


Figure 55. - Effect of carbon dioxide content of raw gas on triethanolamine scrubbing rates.

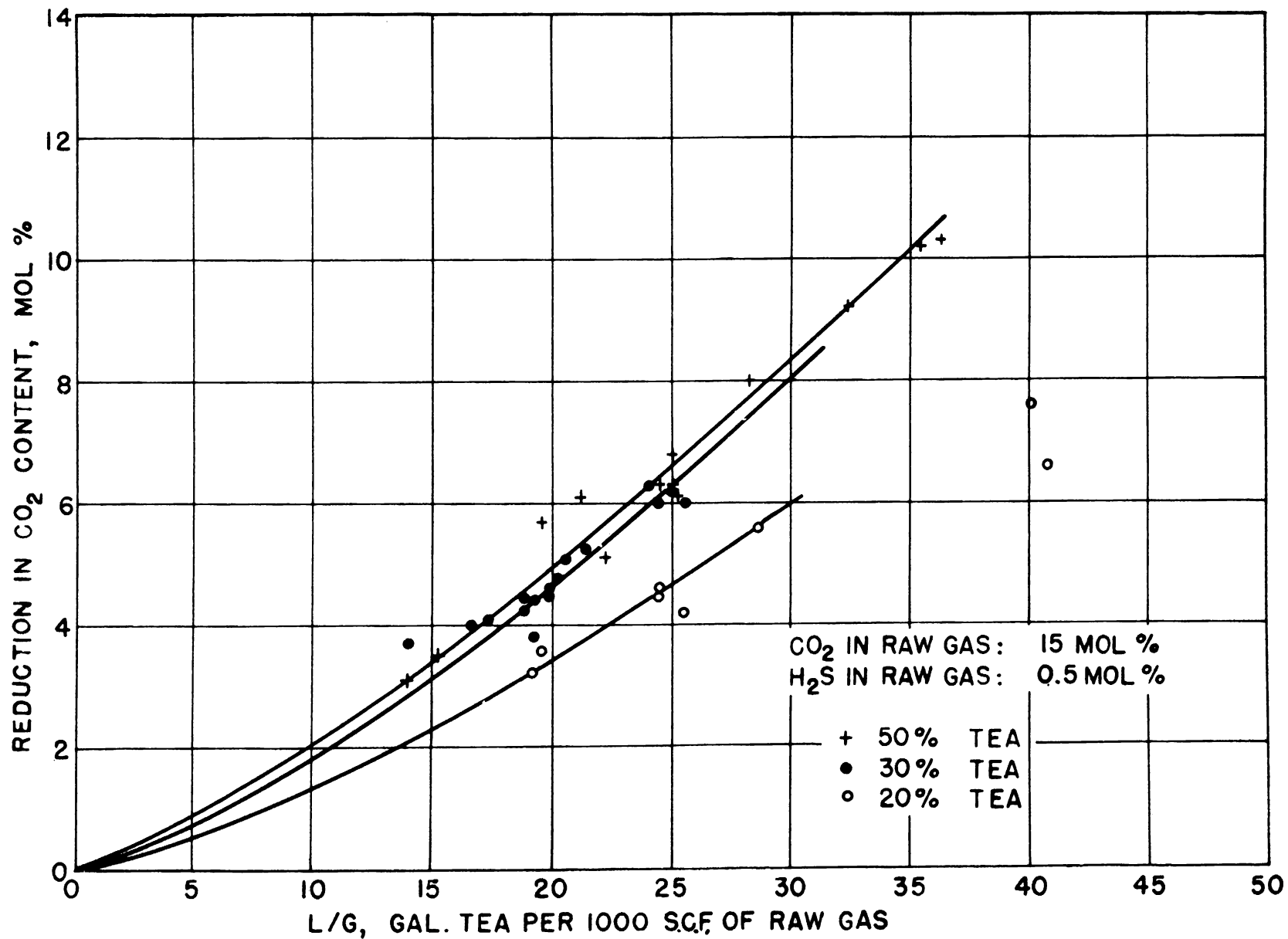


Figure 56. - Effect of triethanolamine scrubbing rates on removal of carbon dioxide.

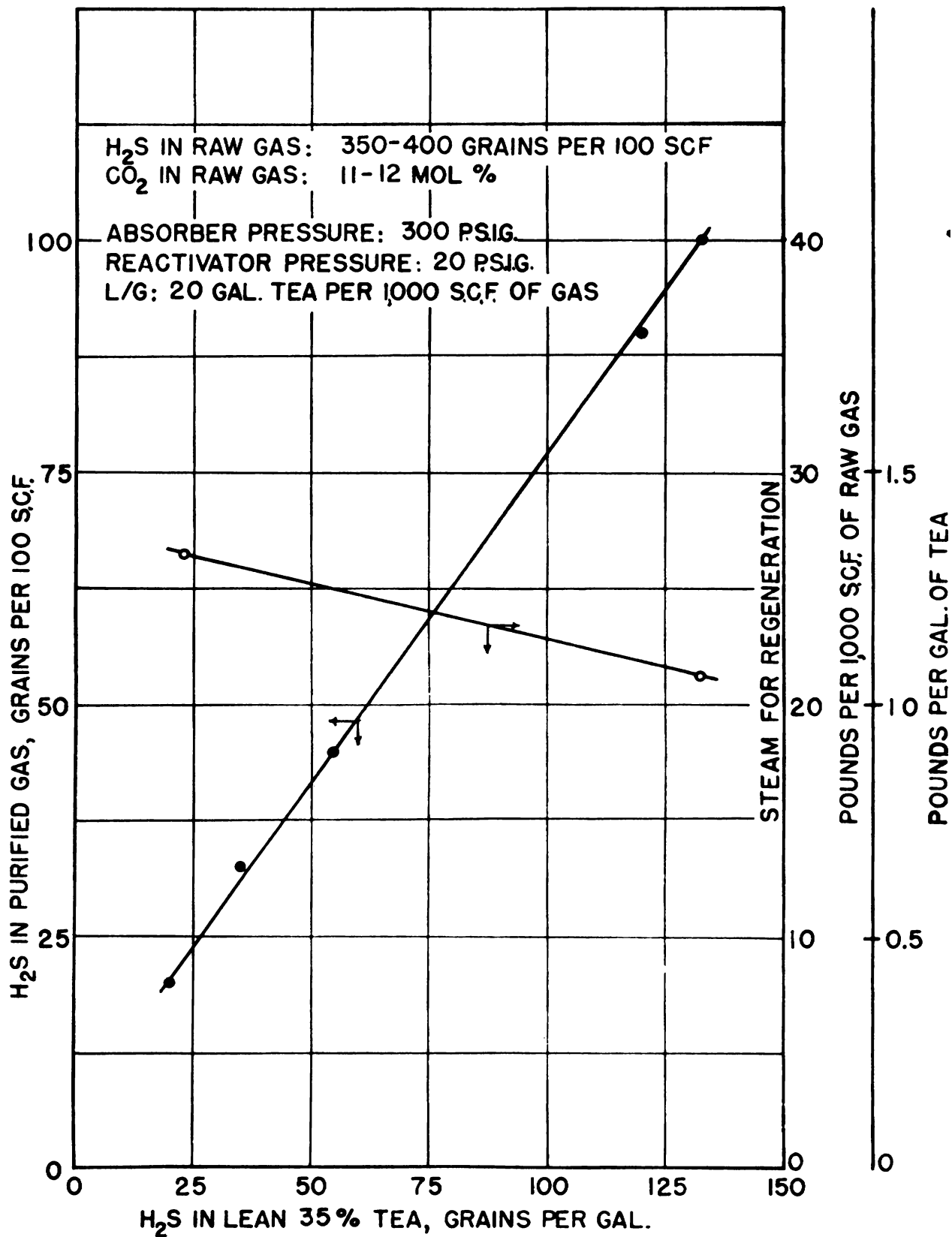


Figure 57. - Effect of steam used for regeneration on hydrogen sulfide concentration in lean triethanolamine solution.

Operation of Pilot Plant

The gas-purification research program at Morgantown always contemplated the necessity of including sulfur recovery as a feature of the gas-purification system in any large commercial plant. This was based not only on the important credits resulting from the sale of byproduct sulfur, but on the assumption that venting appreciable amounts of sulfur in one form or another could not be tolerated. In view of the critical supply situation of sulfur today, the need for sulfur recovery is evident.

Numerous pilot-plant runs have been made, with the primary object of studying the effectiveness of various solutions in selectively removing hydrogen sulfide from a gas containing a relatively large amount of carbon dioxide. Among the absorbents studied have been triethanolamine, sodium carbonate, potassium carbonate, and tripotassium phosphate. It was desirable also to obtain enough data so that cost estimates could be made on the purification of gases having various compositions. A study was made of the effect of various concentrations of solutions, the effect of varying concentrations of carbon dioxide and hydrogen sulfide in the raw gas on the rate of circulation of the solution, the effect of organic sulfur compounds on the purifying solution, the effect of scrubbing rates on residual hydrogen sulfide in the gas, and the foaming characteristics of the scrubbing medium.

Data from 37 runs in which triethanolamine was used have been correlated and the data are presented graphically in figures 55, 56, and 57.

Figure 55 shows the effect of carbon dioxide concentration in the raw gas on triethanolamine scrubbing rates. Figure 56 shows the effect of scrubbing rates of 20, 30, and 50 percent triethanolamine on the removal of carbon dioxide. Although the curves in figure 56 are for a raw gas containing 15 percent carbon dioxide, they have been found to be accurate enough through the range of 5 to 25 percent carbon dioxide if the abscissa (carbon dioxide removed) is increased by 0.1 percent for each additional 1.0 percent carbon dioxide in the raw gas.

As the steam used in regenerating fouled absorbents constitutes the greatest part of hydrogen sulfide removal costs, pilot-plant data were obtained on the amount of steam required to give various concentrations of hydrogen sulfide in a lean 35-percent triethanolamine solution. During these pilot-plant runs, the liquid:gas ratio was held constant, so that a correlation could be obtained between the hydrogen sulfide content of the lean solution and the hydrogen sulfide content of the purified gas leaving the absorber. These data, plotted in figure 57, were obtained during the initial runs with triethanolamine when the reactivator was operated at a pressure of 20 p.s.i.g. Although the steam consumption and hydrogen sulfide content of the lean solution will vary with reactivator pressure, the relationship between hydrogen sulfide in solution and hydrogen sulfide in the purified gas will hold true.

The potassium phosphate process for selective removal of hydrogen sulfide is being studied at present in the pilot plant. When using triethanolamine and a raw gas containing 350 grains of hydrogen sulfide per 100 cu. ft. and 15 percent carbon dioxide, an acid gas containing about 10 percent hydrogen

sulfide was obtained. Data thus far obtained on the phosphate process indicate that, using this same gas, an acid gas having a hydrogen sulfide content of about 20 percent can be obtained.

Under a cooperative agreement with the Southern Natural Gas Co., pilot-plant runs were made to study removal of carbon dioxide from gas using diethanolamine. Data from these runs are plotted in figure 58. These curves show the reduction in the carbon dioxide content of a gas when various solution rates of 20, 30, and 40 percent diethanolamine are used.

In addition to the removal of hydrogen sulfide and carbon dioxide, pilot-plant runs have been made in which the organic sulfur compounds have been removed from raw synthesis gas with "CW" activated carbon. Results from bench-scale experiments using this carbon were reported in the Annual Report for 1950. The results obtained in the pilot plant, as well as those in the Demonstration Plant, corroborated those obtained in the laboratory.

By first removing selectively the bulk of the hydrogen sulfide from raw synthesis gas, removing the residual hydrogen sulfide with iron oxide, and finally removing all the organic sulfur with activated carbon, it has been possible in the pilot plant to reduce the sulfur content of synthesis gas to less than 0.1 grain per 100 cubic feet. In fact, during most of the pilot-plant runs, the sulfur content of the purified gas has been less than 0.05 grain per 100 cubic feet.

Underground Gasification Project, Gorgas, Ala.

The Bureau of Mines and the Alabama Power Co. have jointly conducted field-scale experimentation on the underground gasification of coal at Gorgas, Ala., since 1946. Until February 1951 the program included the construction and operation of two field-scale experiments, the first of 50 days continuous operation and the second of 22 months continuous operation. A third experiment was started in the latter part of June 1951 and is being continued at present.

By underground gasification of coal it may be feasible to produce cheap gas for the production of synthetic liquid fuels or for the generation of power. It may be possible by this means also to exploit coal deposits that are not now mined because of thinness of beds, presence of mineral impurities, or difficult mining conditions.

In the first two experiments, the principles of the "stream method" of underground gasification were utilized wherein air (or oxygen) and steam flow past a coal face and make contact with it. The exposed face is the full thickness of the coal bed; and, as the carbonaceous material is gasified, the face recedes. Successful operation of the U-shaped and straight-line passages, which were employed, depended upon proper roof action, wherein the roof would fuse and slump in front of the reacting coke face and force contact between it and the gas-making fluids. The objectives were to determine the quantity of coal that can be gasified in a given initial combustion zone; to ascertain the quality and quantity of the product gases generated; to obtain information regarding the effect of heat on the overlying strata; and to develop fundamental

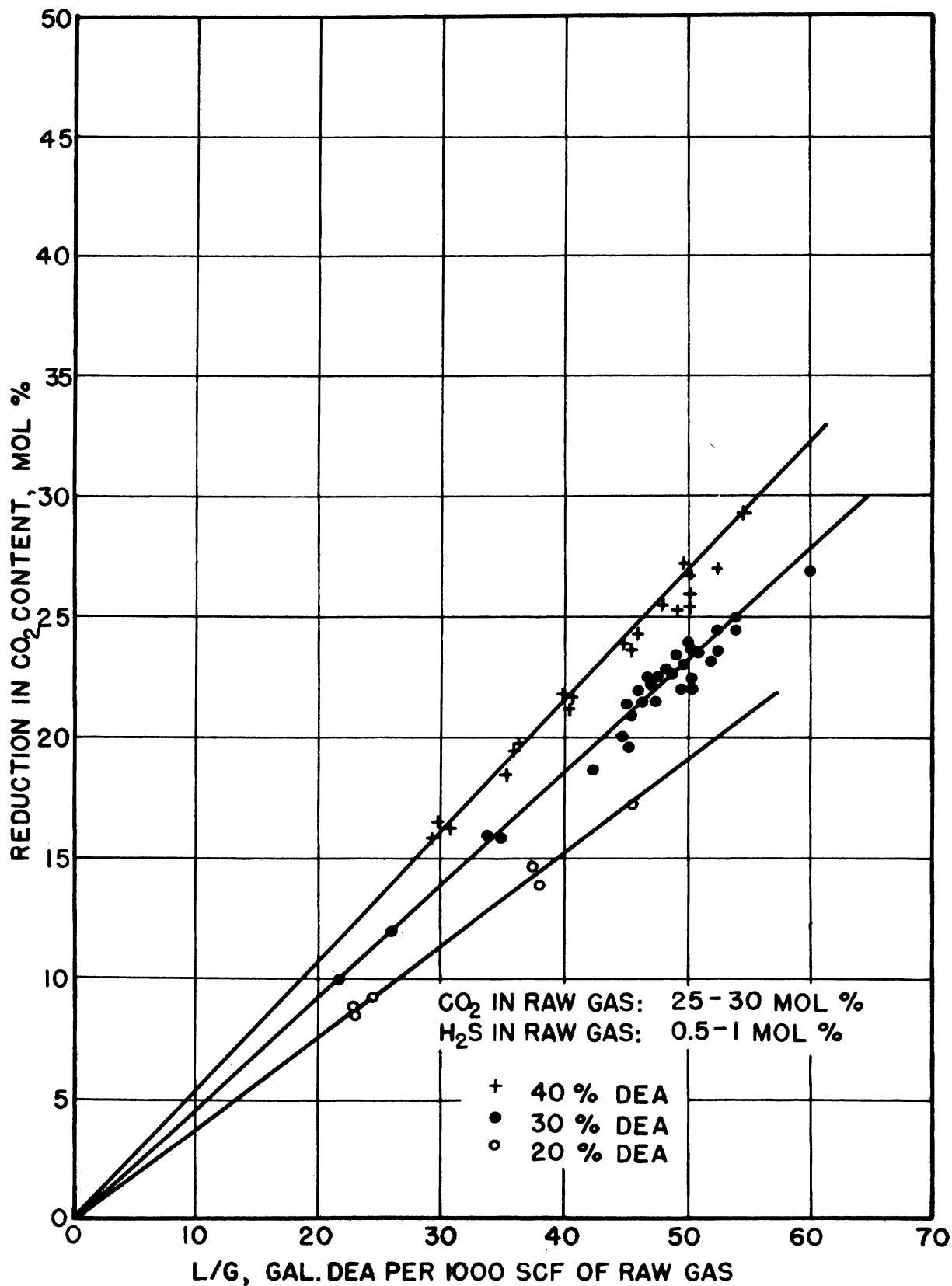


Figure 58. - Effect of diethanolamine scrubbing rates on removal of carbon dioxide from gas.

technical and economic information with regard to the choice of plant sites, installation, and operating procedures.

During the second experiment, 10,500 tons of moisture- and ash-free coal was consumed underlying an area of approximately 2 acres adjacent to the original 1,450 foot entry. Up to the time the project was discontinued, no difficulty had been experienced in maintaining combustion, and no absolute limit had been determined as to the quantity of coal that could be gasified from the original opening. It was part of the original plan of this second experiment to extend gasification to cover a large area of coal bed by providing new inlets and outlets through drilling boreholes off the line of the original entry and tangent to the perimeter of the burned-out area. This was done in the course of the experiment, and it was found that the gasification area could be extended. It appears that there is no definite limit to the area of coal bed that may be exploited in this manner.

During much of the operation, the energy of the coal was brought out of the ground as sensible heat in the product gases. At intervals during the 22 months of operation, a combustible gas was obtained. When boreholes were drilled tangent to the perimeter of the burned-out area, subsequent operation resulted in production of gas ranging from 90 to 150 B.t.u. per cu. ft. Gas of this quality was obtained for short periods, following which free oxygen appeared in the effluent gas, and the heating values diminished to 30 B.t.u. per cu. ft.

Throughout the entire experiment, it was evident that efficient contact between air and the coal faces was required to produce good-quality gas. In consequence, much of the experimental effort was directed toward improving efficiency of contact. Dry sand fluidized with air and injected into voids near the original entries was partly successful. Construction of new boreholes tangent to the coal faces, as noted above, resulted in excellent contact for short periods. Operation with increased area of coal face, achieved by use of double entries or by lengthening of the passage traversed underground, indicated only slight improvement of contact efficiency.

Experiments were conducted to determine optimum rates of air input in the existing system. Little variation in gas quality was observed in the range 4,000 to 7,500 c.f.m.; but, at lower rates, steam generated from ground water appeared in increased concentration. The initial effect of the steam was to increase the calorific value of the gas by production of hydrogen and carbon monoxide. Following this, the generation of steam and its reaction with the incandescent carbon brought about cooling of the underground system and resulted in steady deterioration of gas-making conditions. In view of the moisture effects, therefore, rates of air input for a given system must be maintained at a level at which the moisture concentration is not harmful. The minimum heat loss underground was experienced when blasting was done in the same direction for long periods at high rates of air input.

Leakage from the underground system increased with time and with enlargement of the area of coal consumed. The mechanism of the leakage is not known. No appreciable gas outflows were found at the surface. Tests made toward the end of the experiment showed that leakage was slight from the younger sections

but was very serious from the older, where the coal had been consumed over a wide area.

After the experiments were completed, the fire was extinguished and the underground area cooled by flooding with water. At the end of 7 weeks of flooding, 4.4 million gallons of water had been pumped underground; of this amount, 2.4 million gallons had been discharged as steam. The steam was accompanied by approximately 10 percent of its volume of gas, consisting mostly of products of the reaction between steam and hot carbon. Ten million gallons of water were put underground in 14.5 weeks, and the elevation of water recorded in the boreholes was sufficient to cover the coal bed over the active combustion area. Measurements in various boreholes and test holes indicated that the average temperature near the coal-bed horizon was 200° F.

These first two experiments required underground mining operations in preparing the "U"-shaped and straight-line passages employed. This is both expensive and time consuming. Therefore, the investigation of other methods for preparing the underground system is warranted. For several years the Sinclair Coal Co. and the Missouri School of Mines have been experimenting at Hume, Mo., in connecting pairs of boreholes at the level of a coal bed by inserting electrodes in the coal and passing a current between them. The object was to establish an electrical connection and then carbonize enough coal electrically to permit the flow of air or other gas-making fluids through the system. These experiments have indicated that it is possible to make such a connection.

The major difficulty encountered at Gorgas during the second experiment was inability to enforce contact between gas-making fluids and the coal faces. For these reasons it was decided to develop a new system using electrolinking (see figure 61) as a method of preparing the underground workings and, as the system between two connected boreholes deteriorates during operation, to add more sections, each having a small cross-sectional area, to the original system and thus eliminate underground mining and maintain good contact.

Figure 59 shows a vertical section of the system that was constructed to utilize these principles. The air compressors and piping already at Gorgas were modified for use in the new experiment. The electrical equipment, consisting primarily of a 500 kv.-a. autotransformer fitted with variable voltage taps in 100-volt steps from 200 to 1,800 volts, previously used by the Sinclair Coal Co. at Hume, Mo., was obtained under a cooperative agreement between the Bureau and the company and installed at Gorgas. Additional substation capacity also was provided.

The electrolinking experimentation was performed in the American coal bed rather than the Pratt which had been employed in all previous work at Gorgas. This bed lay under almost 50 feet of additional cover, which included fire clay and sandstone, and it was believed that it would permit the installation of a tighter system. The American bed at this location, as shown in figure 59, appears thicker than the Pratt bed. However, this is due to the presence of fire clay and carbonaceous shale partings. Actually the American coal is slightly thinner than the Pratt.

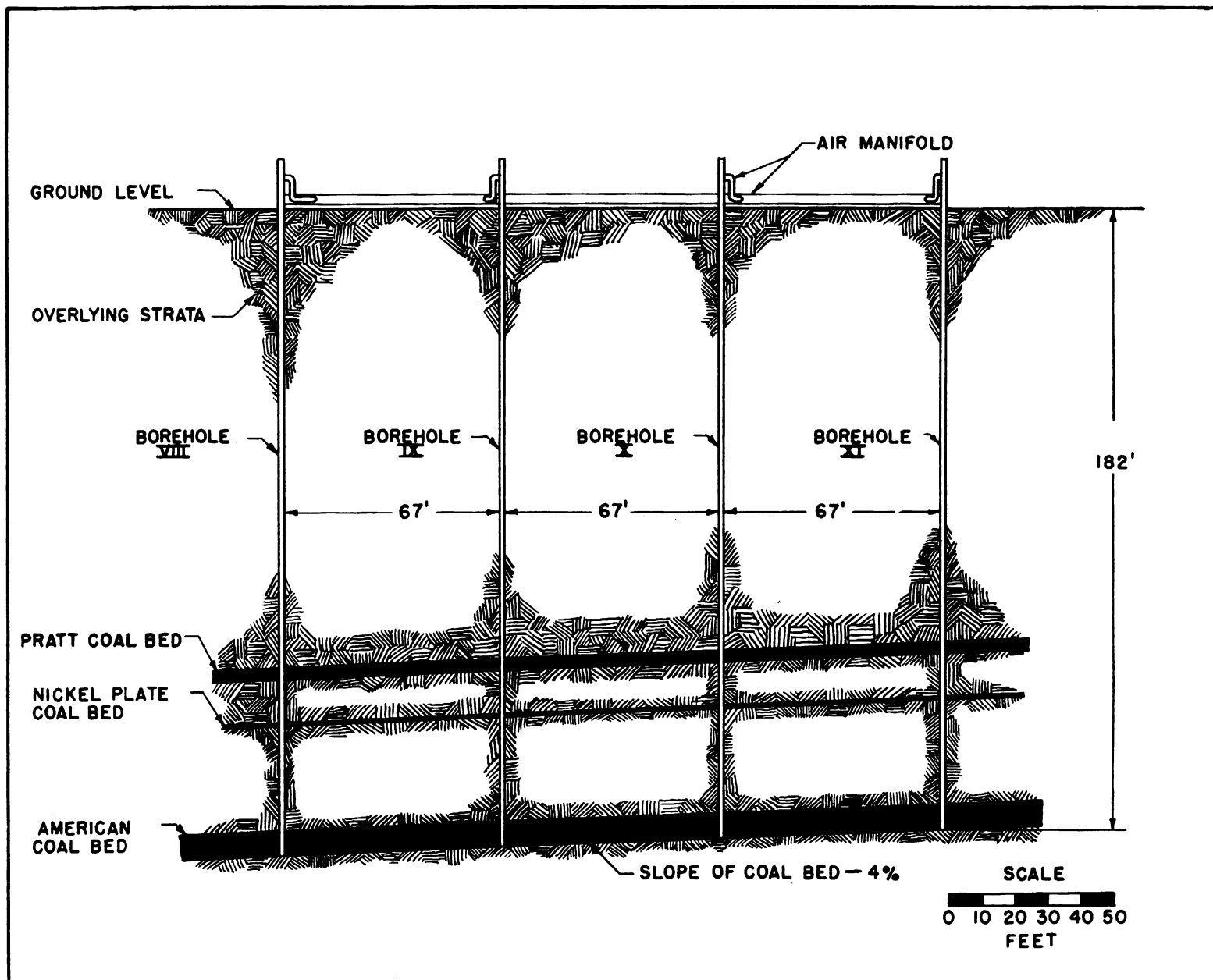


Figure 59. - Vertical section of electrolinking underground gasification experiment.

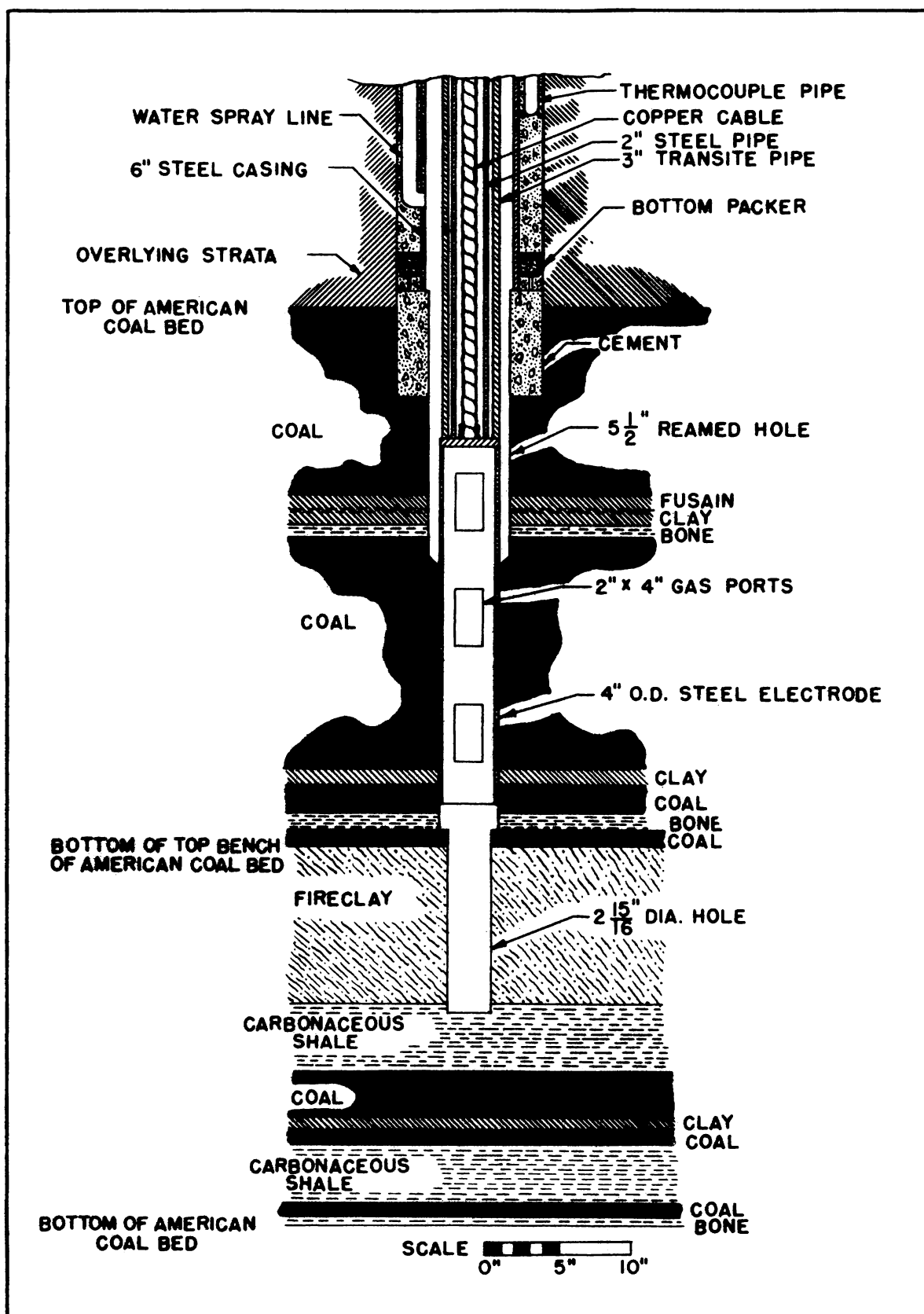


Figure 60. - Installation of electrode in coal bed.



Figure 61. - Burning the gases produced in electrolinking gasification experiment.

Figure 60 shows a typical electrode installation in the coal bed. A 10-inch-diameter borehole was drilled from the surface to the top of the bed. Six-inch steel pipe casing was placed, a water spray line and a thermocouple well were installed, and the annulus between the casing and the strata was filled with cement grout under pressure to seal cracks and crevices in the strata. The coal bed was cored with an NX diamond bit to locate partings and then cored with a 4-inch diamond bit to seat the 4-inch-diameter electrode. At the top of the electrode, the 4-inch hole was reamed to 5-1/2 inches to permit passage of gases formed during the electrolinking. The electrode stem was encased in transite pipe to insulate it from the walls of the hole.

Construction of the installation was completed in June, and electrolinking was begun on the 28th. A potential was applied on the electrodes in boreholes IX and X. On the following day, a potential was applied on electrodes at boreholes VIII and XI. Table 21 gives the results obtained. At the end of the periods given in table 21, arcing occurred between the electrode stems and the casing of the boreholes. Current flow between pairs of electrodes was continued for approximately 2 weeks. Arcing prevented efficient application of current over an interval long enough to carbonize enough coal to reduce the underground resistance to fluid flow to a good operating level. However, electrolinking did increase the permeability of the coal bed, and paths were established between boreholes VIII and IX and boreholes X and XI. Some increase in permeability was obtained between boreholes IX and X, but this was not enough to develop the system in this section further.

TABLE 21. - Electrolinking of boreholes

Time, hours	Potential, volts	Current, amperes	Resistance, ohms
Electrodes in boreholes IX and X			
0	1,800	0 - 110	-
.5	1,960	120	15.3
1.0	1,960	115	16.6
2.0	2,520	210	12.0
4.0 to 16.0	1,380 - 1,840	290 - 320	4.7 - 5.6
16.5	1,280	460	2.8
17.5	1,280	480	2.7
Electrodes in boreholes VIII and XI			
0.25	1,960	70	34.7
.75	1,960	90	22.2
1.25	1,960	101	18.6
3.75	2,500	155	16.7
4.75	2,500	190	13.0
5.75	2,500	215	11.7
6.75	2,500	248	9.8
8.75	2,480	263	9.2
9.75	2,480	292	8.1
10.75	1,820	275	6.5

Boreholes IX and X are 67 feet, center to center, while boreholes VIII and XI are 200 feet. Table 21 shows that length has little effect on the difficulty of establishing an electrical path in the coal bed. Distance does increase the electrical requirements of the system, for more power is required to carbonize the increased quantity of coal. Approximately 7,500 kw.-hr. were required to reduce the resistance between IX and X from an initial value of 32 ohms to 2.7 ohms and 5,000 kw.-hr. to reduce the resistance between VIII and XI from 44 ohms to 6.5 ohms. The power factor for the system varied between 0.95 and 1.00 during this phase of the work.

The original plan of operation called for development of the section between boreholes IX and X, followed by gasification with air until deterioration occurred. The section between VIII and IX was to be added to the system, air injected at X and the products removed at VIII. Such operation would permit use of new coal and insure good contact between reactants. Upon deterioration of the section between VIII and IX or when reversal of flow was required, the section between X and XI was to be used in a similar manner.

During and following the application of electric power, air at pressures up to 100 p.s.i.g. was injected at the various boreholes in order to start gasifying the coke formed underground. It was found that the section between VIII and IX was in the best condition for operation, and this section was used for gasification first. Arcing of electrodes had choked the original boreholes with debris, and it was necessary to drill new holes at the same locations.

In the 44-day period ending August 11, air injection using various pairs of boreholes was attempted. The input air varied from 95 to 365 c.f.m. at pressures of 32 to 100 p.s.i.g. The calorific value of the effluent gases averaged 186 B.t.u. per cubic foot and generally varied from 80 to 300 B.t.u. The high heating value was usually due to methane from coal distillation products, but during one 123-hour portion of the period the carbon monoxide content averaged 13.2 percent, indicating that gasification was taking place. During this period, the volume of the effluent gases was small, and a large fraction of the air pumped underground was not accounted for.

In the 24-day period from August 11 to September 4, the section between boreholes VIII and IX was operated with the air injected at VIII and the outlet at IX. During the first 6 days, the air input averaged 199 c.f.m. at 46 p.s.i.g.; the calorific value of the effluent gases averaged 97 B.t.u. per cubic foot; and 24 percent of the entering air was accounted for in the products. During the next 10 days operation, the air input averaged 301 c.f.m. at 75 p.s.i.g.; the calorific value of the effluent gases averaged 110 B.t.u. per cubic foot; and 45 percent of the input air was accounted for in the products. In the final 8 days of the period, the air input averaged 306 c.f.m. at 51 p.s.i.g.; the calorific value of the effluent gases averaged 130 B.t.u. per cubic foot; and 93 percent of the input air was accounted for in the products. The 24-day period was characterized by an opening up of the underground system, increasing temperature level, and good contact between the reactants resulting in the production of a good quality product, especially during the latter part of the period. The high pressure drop was due in part to the resistance to fluid flow at the horizon of the coal bed and in part to the

condition of borehole VIII, which was partly choked with debris from electro-linking. Borehole IX at this time had been redrilled, but borehole VIII was not yet repaired. During the first part of the period, air was lost by leakage from the underground system, and in the latter part the underground system had opened up enough to remedy this effect.

On September 4 the direction of flow was reversed because of the rising temperature at the outlet, and until the 18th the system was operated with the outlet at borehole VIII and the inlet at IX. The calorific value of the product gases averaged 87 B.t.u. per cubic foot, the system leakage was high as a result of the resistance at borehole VIII. From September 18 until October 30, the system was operated by alternating the direction of flow. During a total of 17 days, the air input was at VIII, with the output at IX. The calorific value of the effluent gases averaged 88 B.t.u. per cubic foot, and good contact between the reactants was maintained. The pressure drop over the system increased, and paralleling this effect leakage increased.

In the immediate future it is planned to open up the system between boreholes IX and XI by inserting new electrodes and applying the electro-linking technique. The experiment has shown that the electro-linking technique can be employed and a system set up for underground gasification whereby underground mining can be eliminated. Further, where good reactant contact is maintained good quality gaseous products can be produced. Better electrode installation, it is believed, will materially decrease the time required for development and result in larger throughputs than have been obtained.

APPENDIX. - BIBLIOGRAPHY OF PAPERS AND REPORTS PRESENTED OR PUBLISHED IN 1951

PROCESSING, Coal-to-Oil Demonstration Plants, Louisiana, Mo.

1. BALCERZAK, C. E., and SKILLERN, J. A. Performance of High-Pressure Instruments in the Bureau of Mines' Synthetic Fuels Demonstration Plant. Am. Soc. Mech. Eng. Tech. Paper 51-PET-7, September 1951, 15 pp.
2. BATCHELDER, H. R., and INGOLS, H. A. Performance of a Pebble-Heater-Type Steam Superheater. Bureau of Mines Rept. of Investigations 4781, 1951, 16 pp.
3. DONOVAN, J. T., LEONARD, B. H., and MARKOVITS, J. A. Design and Development of High-Pressure Injection Pumps for Hydrogenation Service. Am. Soc. Mech. Eng. Tech. Paper 51-A-71, November 1951, 22 pp.
4. DOUGHERTY, R. W. A Survey on the Hydraulic Transportation of Coal. Bureau of Mines Rept. of Investigations 4799, 1951, 22 pp.
5. HIRST, L. L., DRESSLER, R. G., and BATCHELDER, HOWARD R. Bureau of Mines Completes Gas-Synthesis Plant. Crane Valve World, vol. 48, No. 1, 1951, pp. 98-103.

RESEARCH AND DEVELOPMENT, Coal-to-Oil Laboratories and Pilot Plants,
Bruceton and Pittsburgh, Pa.

1. ANDERSON, R. B., FRIEDEL, R. A., and STORCH, H. H. Fischer-Tropsch Reaction Mechanism Involving Stepwise Growth of Carbon Chain. Jour. Chem. Phys., vol. 19, 1951, pp. 313-319.
2. ANDERSON, R. B., HOFER, L. J. E., COHN, E. M., and SELIGMAN, B. Studies of the Fischer-Tropsch Synthesis, IX. Phase Studies of Iron Catalysts in the Synthesis. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 944-946.
3. CLARK, E. L., HITESHUE, R. W., KANDLINER, H. J., and MORRIS, B. Hydrogenation of Shale Oil Coker Distillate. Ind. Eng. Chem., vol. 43, 1951, pp. 2173-2178.
4. COHN, E. M. Bureau of Mines Research on Synthetic-Liquid-Fuels Processes. Bibliography of Technical Reports, U. S. Department of Commerce, Office of Technical Services, vol. 15, 1951, pp. 65-66.
5. COHN, E. M., and HOFER, L. J. E. Mode of Transition from Hagg Iron Carbide to Cementite. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 4662-4664.
6. _____ Preparation of Iron Carbides. U. S. Patent 2,535,042, December 26, 1950.
7. CROWELL, J. H., BENSON, H. E., FIELD, J. H., and STORCH, H. H. Fischer-Tropsch Oil Circulation Processes. Ind. Eng. Chem., vol. 42, 1950, pp. 2376-2384.
8. FELDMAN, J., PANTAGES, P., and ORCHIN, M. Purification and Freezing Point of Phenanthrene. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 4341-4343.
9. FELDMAN, J., PANTAZOPOLOS, P., PANTAZOPOLOS, G., and ORCHIN, M. The Design, Construction, and Operation of a Distillation Laboratory for the Synthetic Liquid Fuels Program. Bureau of Mines Rept. of Investigations 4764, 1951, 4 pp.
10. FRIEDEL, R. A. Infrared Spectra of Phenols. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 2881-2884.
11. GOLUMBIC, C. Separation and Analysis of Phenols by Countercurrent Distribution. Anal. Chem., vol. 22, 1950, p. 508.
12. _____ Liquid-Liquid Extraction Analysis. Anal. Chem., vol. 23, 1951, pp. 1210-1218.
13. GOLUMBIC, C., and GOLDBACH, G. Partition Studies VI. Partition Coefficients and Ionization Constants of Methyl-Substituted Anilines. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 3966-3967.
14. GOLUMBIC, C., and WELLER, S. Measurement of Large Partition Coefficients by Interchange Extraction. Anal. Chem., vol. 22, 1950, pp. 1418-1419.
15. GRASS, R. C. (editor). Process Development in the Hydrocarbon Synthesis to 1941. Bureau of Mines Inf. Circ. 7593, 1951, 41 pp.
16. _____ Bench-Scale Studies of the Fischer-Tropsch Synthesis over Iron, Nickel, and Nickel-Cobalt Catalysts (Japan). Bureau of Mines Inf. Circ. 7611, 1951, 26 pp.
17. GRASS, R. C., and STORCH, H. H. Synthetic Liquid Fuels. Contribution to: FIELDNER, A. C., GAUGER, A. W., and YOHE, G. R. Gas and Fuel Chemistry. Ind. Eng. Chem., vol. 43, 1951, pp. 1039-1048.

18. HALL, W. K., TARN, W. H., and ANDERSON, R. B. Studies of the Fischer-Tropsch Synthesis, VIII. Surface Area and Pore Volume Studies of Iron Catalysts. *Jour. Am. Chem. Soc.*, vol. 72, 1950, pp. 536-543.
19. HOFER, L. J. E., and COHN, E. M. Some Reactions in the Iron-Carbon System; Application to the Tempering of Martensite. *Nature*, vol. 167, 1951, pp. 977-978.
20. HOFER, L. J. E., and PEEBLES, W. C. X-Ray Diffraction Patterns of Solid Aromatic Hydrocarbons. *Anal. Chem.*, vol. 32, 1951, pp. 690-695.
21. HUSACK, R., and GOLUMBIC, C. Characterization of the Phenolic Fraction of Coal-Hydrogenation Asphalt. *Jour. Am. Chem. Soc.*, vol. 73, 1951, pp. 1567-1571.
22. KANDINER, H. J., HITESHUE, R. W., and CLARK, E. L. Catalyst Evaluation and Middle-Oil Preparation in an Experimental High-Pressure Coal Hydrogenation Plant, Part I. *Chem. Eng. Prog.*, vol. 47, 1951, pp. 392-396.
23. LECKY, J. A., HALL, W. K., and ANDERSON, R. B. Adsorption of Water and Methanol on Coal. *Nature*, vol. 168, 1951, pp. 124-125.
24. LEVA, M. Packed-Tube Heat Transfer. *Ind. Eng. Chem.*, vol. 42, 1950, pp. 2498-2501.
25. _____ Elutriation of Fines from Fluidized Systems. *Chem. Eng. Progress*, vol. 47, 1951, pp. 39-45.
26. LEVA, M., and WEINTRAUB, M. Fluid Dynamics. *Ind. Eng. Chem.*, vol. 43, 1951, pp. 90-99.
27. MANES, M., HOFER, L. J. E., and WELLER, S. Classical Thermodynamics and Reaction Rates Close to Equilibrium. *Jour. Chem. Phys.*, vol. 18, 1950, pp. 1355-1361.
28. MYLES, M., FELDMAN, J., WENDER, I., and ORCHIN, M. Fractionating Efficiency of Various Packings. *Ind. Eng. Chem.*, vol. 43, 1951, pp. 1452-1456.
29. ORCHIN, M. Steric Effects in Complex Compound Formation. *Jour. Organic Chem.*, vol. 16, 1951, pp. 1165-1169.
30. ORCHIN, M., and REGGEL, L. Synthesis of Fluoranthene and Its Derivatives. U. S. Patent 2,503,292, April 11, 1950.
31. _____ Synthesis of Benzo [j] fluoranthene and Benzo [k] fluoranthene. *Jour. Am. Chem. Soc.*, vol. 73, 1951, pp. 436-442.
32. _____ Aromatic Cyclodehydrogenation, X. Studies on Ring Oxygen Compounds. Dinaphtho (1,2,1',2') furan. *Jour. Am. Chem. Soc.*, vol. 73, 1951, 1877-1878.
33. _____ A Synthesis of Fluoranthene by Cyclodehydration. *Jour. Am. Chem. Soc.*, vol. 73, 1951, pp. 2955-2956.
34. ORCHIN, M., and WOOLFOLK, E. O. Synthesis of Di-Aryl Cyclic Ethers. U. S. Patent 2,566,357, September 4, 1951.
35. ORCHIN, M., REGGEL, L., and FRIEDEL, R. A. The Anomalous Reaction of 1-Tetralone with o-Tolylmagnesium Bromide. *Jour. Am. Chem. Soc.*, vol. 73, 1951, pp. 1449-1454.
36. SCHLESINGER, M., CROWELL, J. H., and LEVA, M. Fischer-Tropsch Synthesis in the Slurry Phase. *Ind. Eng. Chem.*, vol. 43, 1951, pp. 1474-1479.

37. STORCH, H. H. Book review of "Progress in Coal Science" (D. H. BANCHAM, editor). Jour. Phys. Colloid Chem., vol. 55, 1951, pp. 1109-1110.
38. WELLER, S., Recovery of Light Elemental Gases. United States Patent 2,540,152, Feb. 6, 1951.
39. WELLER, S., and PELIPETZ, M. G. Coal Hydrogenation Catalysts. Studies of Catalyst Distribution. Ind. Eng. Chem., vol. 43, 1951, pp. 1243-1246.
40. _____ Catalysts in Liquid-Phase Coal Hydrogenation. Proceedings of the Third World Petroleum Congress, The Hague, Netherlands, June 3, 1951. Sec. IV, subsec. I, Prepr. 7.
41. WELLER, S., PELIPETZ, M. G., and FRIEDMAN, S. Kinetics of Coal Hydrogenation. Conversion of Asphalt. Ind. Eng. Chem., vol. 43, 1951, pp. 1572-1575.
42. _____ Kinetics of Coal Hydrogenation. Conversion of Anthraxylon. Ind. Eng. Chem., vol. 43, 1951, pp. 1575-1579.
43. WELLER, S., and STEINER, W. A. Engineering Aspects of Separation of Gases. Chem. Eng. Prog., vol. 46, 1950, pp. 585-590.
44. _____ Separation of Oxygen from Gas Mixtures Containing the Same. United States Patent 2,540,151, February 6, 1951.
45. WENDER, I., FRIEDEL, R. A., and ORCHIN, M. Ethanol from Methanol. Science, vol. 113, 1951, pp. 206-207.
46. WENDER, I., GREENFIELD, H., and ORCHIN, M. Chemistry of the Oxo and Related Reactions, IV. Reductions in the Aromatic Series. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 2656-2658.
47. WENDER, I., LEVINE, R., and ORCHIN, M. Chemistry of the Oxo and Related Reactions, II. Hydrogenation. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 4375-4378.
48. WENDER, I., ORCHIN, M., and STORCH, H. H. New Modifications of the Oxo Process. Armed Forces Chem. Jour., vol. 4, 1950, pp. 4-9.
49. _____ Mechanism of the Oxo and Related Reactions, III. Evidence for Homogeneous Hydrogenation. Jour. Am. Chem. Soc., vol. 72, 1950, p. 4842.
50. WILEY, J. L., and ANDERSON, H. C. Bibliography of Pressure Hydrogenation, I. Review and Compilation of the Literature on Pressure Hydrogenation of Liquid and Solid Carbonaceous Materials. Bureau of Mines Bulletin 485, 1950, 306 pp.
51. WIRTH, G. (GRASS, R. C., and KANDINER, H. J., translators). The Evaluation of Converters for Exothermic and Endothermic Catalytic Reactions Occurring Within Narrow Temperature Limits. Bureau of Mines Inf. Circ. 7587, 1950, 13 pp.
52. WOLFSON, M. L., PELIPETZ, M. G., DAMICK, A. D., and CLARK, E. L. Vapor-Phase Hydrogenation. Ind. Eng. Chem., vol. 43, 1951, pp. 536-540.
53. WOOLFOLK, E. O., COLUMBIC, C., FRIEDEL, R. A., ORCHIN, M., and STORCH, H. H. Characterization of Tar Acids from Coal-Hydrogenation Oils. Bureau of Mines Bull. 487, 1950, 56 pp.

RESEARCH AND DEVELOPMENT, Synthesis-Gas Laboratories and Pilot Plants,
Morgantown, W. Va., and Field Tests, Gorgas, Ala.

1. STRIMBECK, G. R., HOLDEN, J. H., ROCKENBACH, L. P., CORDINER, J. B., Jr., and SCHMIDT, L. D. Pilot Plant Gasification of Pulverized Coal with Oxygen and Highly Superheated Steam. Bureau of Mines Rept. of Investigations 4733, 1950, 41 pp.
2. WAINWRIGHT, H. W., and LAMBERT, G. I. A Colorimetric Method for the Determination of Thiophene in Synthesis Gas. Bureau of Mines Rept. of Investigations 4753, 1950, 11 pp.
3. ELDER, JAMES L., GRAHAM, HUGH G. Experiment on Underground Gasification of Coal. Mines Magazine, vol. 40, No. 10, 1950, pp. 107-111, 117, 134.
4. SEBASTIAN, J. J. S., EDEBURN, P. W., BONAR, F., BONIFIELD, L. W., and SCHMIDT, L. D. Laboratory-Scale Work on Synthesis-Gas Production. Bureau of Mines Rept. of Investigations 4742, 1951, 41 pp.
5. STONE, D. E., KANE, L. J., CORRIGAN, T. E., WAINWRIGHT, H. W., and SEIBERT, C. B. Investigation of a Photoelectric Device for the Determination of Low Concentrations of Dust. Bureau of Mines Rept. of Investigations 4782, 1951, 6 pp.
6. BARKER, K. R., SEBASTIAN, J. J. S., SCHMIDT, L. D., and SIMONS, H. P. Pressure Feeder for Powdered Coal or Other Finely Divided Solids. Ind. Eng. Chem., vol. 43, No. 5, May 1951, pp. 1204-1209.
7. ELDER, JAMES L., and WILKINS, E. T. The Underground Gasification of Coal in the U. S. A. An Outline of the Bureau of Mines' Experiments at Gorgas, Alabama. Jour. Inst. Fuel, vol. 24, No. 137, May 1951, pp. 94-99.
8. SCHMIDT, L. D. Synthesis Gas From Pulverized Coal, Oxygen, and Highly Superheated Steam Is Produced in Pilot Plant. Am. Gas Jour., vol. 175, No. 1, July 1951, pp. 10-14, 42.
9. ALBRIGHT, C. W., HOLDEN, J. H., SIMONS, H. P., and SCHMIDT, L. D. Pressure Drop in Flow of Dense Coal-Air Mixtures. Ind. Eng. Chem., vol. 43, No. 8, August 1951, pp. 1837-1840.
10. Descriptive pamphlet "Synthesis Gas Branch, U. S. Bureau of Mines, Morgantown, W. Va.", August 1951, 9 pp.
11. BARKLEY, L. W., CORRIGAN, T. E., WAINWRIGHT, H. W., and SANDS, A. E. A Kinetic Study of the Catalytic Reverse Shift Reaction. Presented before Am. Chem. Soc., New York, N. Y., September 1951. To be pub. in Ind. Eng. Chem.
12. SEBASTIAN, JOHN J. S. Effect of Variables in Powdered Coal Gasification. Presented before Gas and Fuel Division, Am. Chem. Soc., Diamond Jubilee Meeting, New York, N. Y., Sept. 7, 1951.
13. ELDER, JAMES L., FIES, M. H., GRAHAM, HUGH G., MONTGOMERY, R. C., SCHMIDT, L. D., and WILKINS, E. T. The Second Underground Gasification Experiment at Gorgas, Ala. Bureau of Mines Rept. of Investigations 4808, 1951, 72 pp.
14. ELDER, JAMES L., GRAHAM, HUGH G., CAPP, J. P., and EDDY, W. H. The Underground Gasification of Coal. Military Engr., vol. 43, No. 296, November-December 1951, pp. 398-400.
15. ELDER, JAMES L. Resumé of the Second Underground Gasification Experiment at Gorgas, Alabama. Presented before Rocky Mt. Coal-Mining Inst., Salt Lake City, Utah, June 8, 1951, and to be published in Proc. Inst.

