SYNTHETIC LIQUID FUELS

ANNUAL REPORT OF THE SECRETARY OF THE INTERIOR FOR 1950

PART I. - OIL FROM COAL

* * * * * * * * * **Report of Investigations 4770**

UNITED STATES DEPARTMENT OF THE INTERIOR
Oscar L. Chapman, Secretary
BUREAU OF MINES
James Boyd, Director

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Annual Report of the Secretary of the Interior for 1950

Part I. - 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 1950 has been divided into four separate publications. Each has been published by the Bureau of Mines as a Report of Investigations, and the respective titles follow:

R. I. 4770, Part I - Oil from Coal.

R. I. 4771, Part II - Oil from Oil Shale.

R. I. 4772, Part III - Liquid Fuels from Agricultural Residues.

R. I. 4773, Part IV - Oil from Secondary Recovery and Refining.

Identical in each report, the introduction summarizes research progress made in 1950 under the entire Synthetic Liquid Fuels program.

A free copy of any 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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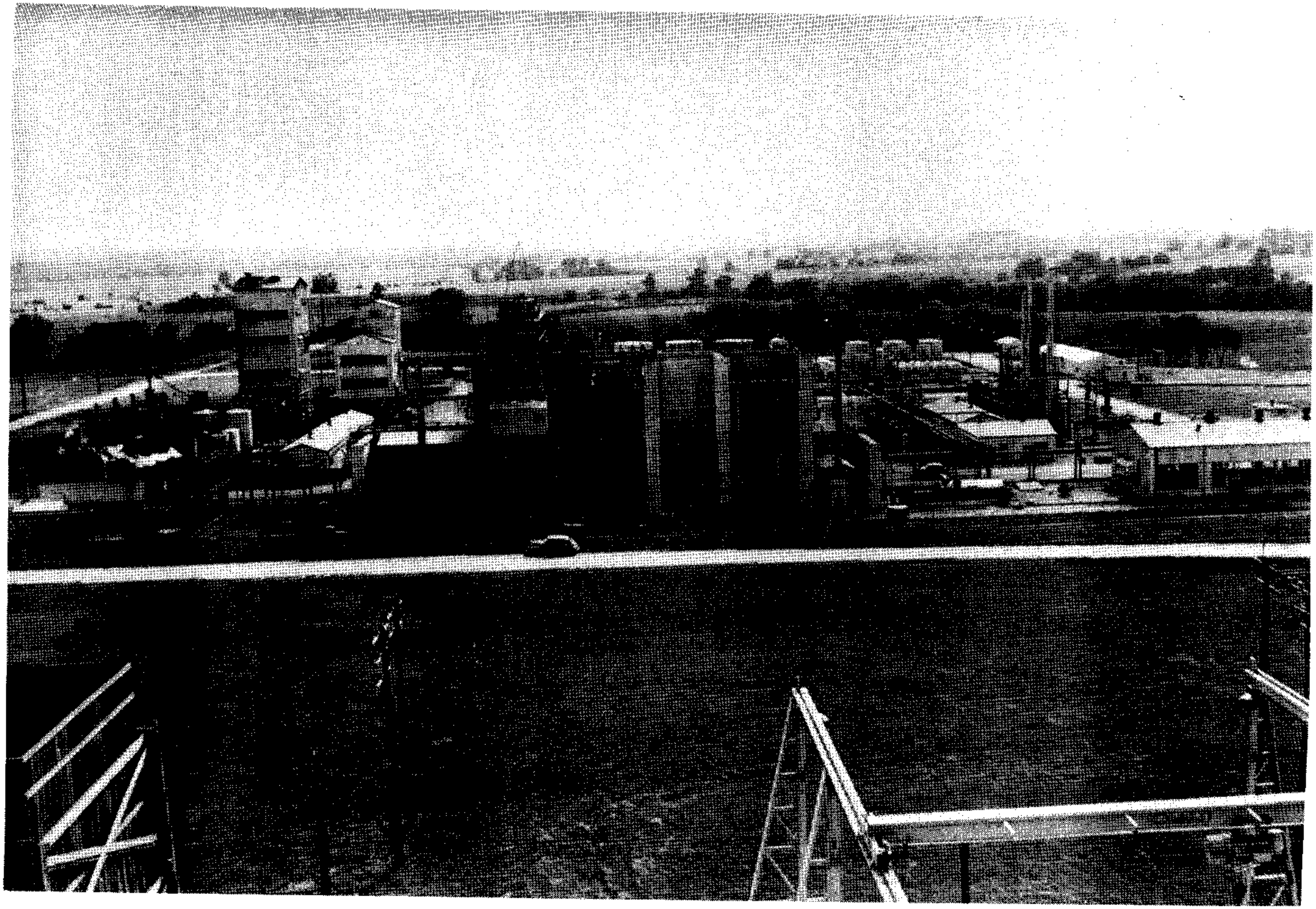

Figure 1. - Coal-Hydrogenation Demonstration Plant near Louisiana, Mo. Stalls in center, refinery and light-oil storage at right, heavy-oil area in left foreground, and coal and paste preparation units in left background.

INTRODUCTION

The United States has not begun commercial operations to tap its largest potential sources of oil supply - oil shale and coal. The reason is that domestic petroleum has been plentiful in the past and liquid products probably could be produced from it at the lowest cost.

In view of the ever-increasing need for petroleum in the United States, the critical international situation threatening foreign supplies, the growing demands for steel, and the heavy costs to industry of constantly discovering and developing new oil fields, it is believed that the prompt development of a synthetic fuel industry based on oil shale and coal is not only requisite to safeguard our oil supply but is an economically sound course for the foreseeable future. To neglect its development is to close our eyes and minds to our own resources at a time when they are needed critically. It also is apparent now that neither the Government nor industry would be taking any considerable economic risk in starting the initial plants, especially as measured against their potential value in meeting critical oil and chemical demands and in building a new industry in the West.

Oil Shale

Owing to research advances in the extensive synthetic liquid fuels program, which has been carried on by industry and the Department of the Interior since 1944, it now is believed that gasoline and oil can be produced from shale at costs close to those for petroleum products. The steel required for oil-shale mines and plants, as well as the capital investment, appears to be less than now required by the petroleum industry for each barrel day of added capacity. Oil shale plants can be built in one to two years and enough reserves can be provided to permit operation at full capacity for 20 or 30 years. This contrasts sharply with petroleum operations in which the average oil field approaches depletion in 10 to 14 years and older fields must be replaced continually by the discovery and development of new reserves.

Progress made in the oil-shale development program during 1950, which is summarized in a later section of this report, greatly strengthened the commercial feasibility of these operations. The shale mining operations were improved further. It is now estimated that the raw shale for one gallon of crude shale oil will cost 1.5 cents, crushed and delivered at the retorting plant. The retorting process has been improved as to both method and cost by the development of the gas combustion retort. This is a simple upright cylindrical vessel that preheats the incoming air, retorts the shale, and condenses the oil given off without the use of water. Single units of the retort can be built with large capacity, and the process is continuous.

The combined research effort of industry and the Government has now developed refining processes for crude shale oil that will yield high quality motor gasoline, jet fuel, diesel oil, and all grades of heating oils. These refining methods have been examined thoroughly both by industry and the Bureau of Mines.

The Department of the Interior, will give its full support to competent organizations or groups of organizations putting forward sound proposals to start commercial operations in this field. The Department believes that it is in the best national interest to push this oil shale program forward as rapidly as possible.

Coal Hydrogenation

The Bureau of Mines Coal-Hydrogenation Demonstration Plant at Louisiana, Mo., now has been in operation for about 1-1/2 years. A completed series of runs on Wyoming coal is described in detail in the body of this report. New runs are now being started on Kentucky coal, and these will be followed by tests on coals from other states. The major product has been gasoline which is being used for test purposes, particularly by the armed forces. Having no counterpart in previous American experience, this new high pressure plant has presented numerous operating problems. Each has been solved as it arose, however, and equipment and operations are modified continuously to improve the plant economy.

The experience gained in this work, combined with records of operating experience from German plants, has been used as a basis for reestimating the initial cost of certain sections of a commercial coal-hydrogenation plant, as well as the cost of the products. This new work is not completed and will not be published until those estimates are reviewed by the Synthetic Liquid Fuels Subcommittee of the National Petroleum Council. At the request of the Secretary of the Interior, this group is working with the Bureau of Mines to develop cost estimates mutually acceptable to industry and the Government on all of the synthetic fuel processes.

At the present time, it appears that the cost of producing gasoline from coal is somewhat greater than it is from shale. In many instances, however, the coal plants will have a material advantage over shale for they can be placed near important consuming centers where product-transportation costs will be relatively low. To some extent, this offsets the advantage of lower production costs for shale products.

The studies of the last two years, however, have brought out one point of major importance in the present emergency: That the amount of steel required for initial construction per barrel per day of gasoline is about the same for coal hydrogenation as it is for petroleum. Also, if a coal hydrogenation plant is used for 20 years, the actual amount of steel consumed per barrel of product made is less than that required for petroleum. These facts may appear surprising, at first glance, but it must be remembered that the oil industry estimates its steel requirements for 1951 at approximately 10 percent of the steel productive capacity of the United States.

During the past few years, demand for such aromatic chemicals as benzene and phenol has outstripped productive capacity. These materials are used in plastics, nylon, insecticides, and many other essential chemical products. Benzene requirements increased still further when the synthetic rubber plants were reopened, for it is used to make styrene which is one of the basic components of synthetic rubber. The shortage of benzene is now acute and its price has been advancing rapidly.

This situation creates favorable economic conditions for the construction and operation of one or two coal-hydrogenation plants. Along with gasoline, such plants can produce a high percentage of aromatic chemicals. A total hydrogenation capacity of 30,000 barrels a day, for example, would increase the country's benzene production by about 80 percent, its phenol output by about 11 percent, and provide substantial amounts of toluene and xylene for aviation fuels, as well as a new source of motor gasoline and liquefied petroleum gas. In addition, about 40,000 tons of sulfur would be recovered each year to help meet growing shortages in this field.

The amount of steel used for the initial plant construction is about the same as required to make these aromatics from petroleum. This approximation includes the steel used for mining and conveying coal to the hydrogenation plants and in the case of petroleum the steel used for producing and transporting the crude oil. At November 1950 prices for the chemicals, gasoline, and other products, a coal-hydrogenation plant would pay out in about 10 years, after provision is made for sales expense, management, interest, taxes, and all direct operating costs.

It must be remembered further that the hydrogenation plants will not compete in time of emergency for raw materials that are already in short supply. In such critical periods, petroleum must fill a vast need for aviation gasoline, motor gasoline, jet fuel, Diesel oil, heating oil, and chemicals. Each of these products becomes increasingly vital during a war and important competing needs clamor to be supplied. While the demands for coal also increase, these can be supplied from the vast resources of the United States alone. During World War II, coal production rose from about 500 million tons per year to a maximum of about 650 million tons. This or a greater expansion can be achieved again when it becomes necessary. The building of hydrogenation plants is the first step to allow coal, the largest fuel reserve in the United States, to begin to carry some of the heavy demands for liquid fuels.

One of the major advantages of coal hydrogenation plants is their great flexibility and control of the type of product. They can be operated to yield a liquid product that is almost entirely aviation gasoline base stock, or aviation and motor gasoline jet fuel and Diesel oil in widely adjustable proportions. Under other operating conditions, they will give a high yield of aromatic chemicals, including aviation gasoline blending agents, and motor gasoline. If desired, they could produce large amounts of Diesel oil and heating oil. This flexibility holds great strategic advantage in time of war. In peacetime such plants again can be operated to supply the products most needed for a civilian economy.

The Department of the Interior will encourage the construction of one or two coal hydrogenation plants. If Government assistance is required in their initial financing, it is believed that these funds will all be recovered with interest in relatively few years. If the prices of aromatic chemicals continue to rise, these plants will be a most profitable business venture.

Gas Synthesis Process (from coal)

The Gas Synthesis process is also to be demonstrated by the Bureau of Mines at Louisiana, Mo. This process differs from hydrogenation in that coal is converted first to a synthesis gas (carbon monoxide and hydrogen) and then to synthetic liquid fuels.

American industry, principally companies representing the oil industry, have been interested in this method, starting with either natural gas or coal as the basic raw material. One commercial plant of 7,000 barrels per day capacity has been constructed by private industry which uses natural gas as the starting material. The Bureau of Mines gas synthesis demonstration plant which uses coal as a raw material will be completed in the early part of 1951.

Designs of commercial plants based on the process from coal are being drawn up and cost estimates are being made. This work will be reviewed by the National Petroleum Council subcommittee.

The studies and demonstration of the Gas Synthesis process from coal are not as far advanced as studies of the coal hydrogenation or the shale processes. Conclusions as to time and degree of commercialization of this process await the completion of studies and demonstration work to be started or now in progress.

A summary of 1950 operations at each of the synthetic liquid fuels laboratories and demonstration plants follows:

Oil from Coal

Demonstration Plants, Louisiana, Mo.

As a proving ground for American coals, equipment, and processing methods, the two Coal-to-Oil Demonstration Plants near Louisiana, Mo. - first of their kind in this country - employ different processes to convert coal and lignite to high-quality synthetic liquid fuels. These are known as the coal-hydrogenation and gas-synthesis processes.

In 1950, its first full year of operations, the Coal-Hydrogenation Demonstration Plant completed five runs with a combined "on-stream" time of about 100 days. In four liquid-phase operations, approximately 3,000 tons of Rock Springs, Wyo., coal was converted into 300,000 gallons of vapor-phase charging stock. Then, in a vapor-phase run of 1-month duration, this oil was processed into a very satisfactory motor gasoline of 78 octane rating (motor method). Arrangements have been made to use the bulk of this product in fleet road tests. This program is in progress and early reports are satisfactory.

Liquid-phase coal hydrogenation runs Nos. 2 and 3, conducted at pressures of 10,000 pounds to the square inch, were hampered seriously by injection pump, instrument, and converter coking difficulties. These troubles were greatly alleviated during liquid-phase runs Nos. 4 and 5, however, by increasing the gas flow through the paste preheater and converters, and by operating the system at 7,500 to 8,000 pounds per square inch.

At the beginning of the vapor-phase run, which was conducted at 10,000 pounds pressure, a cross leak in the feed-product exchanger spoiled the product and necessitated a shutdown. The plant functioned smoothly for the full month after resumption of the run, and good results were obtained. During all runs, the refinery and hydrogen-gas manufacturing areas were operated continuously on a routine basis.

In building the Gas-Synthesis Demonstration Plant, favorable weather, good labor relations, and excellent supervision of the construction workers enabled Koppers Co., Inc., to complete the synthesis and distillation units early in the summer.

Operation of the Linde-Fränkl oxygen plant was routine whenever oxygen was necessary for gasification work.

Test runs were continued in a Koppers powdered-coal gasifier to improve the degree of reaction achieved between carbon and steam. A total of 46 tests was made before the unit was shut down in May. One of these runs was extended over an 11-day period to test the mechanical performance of the unit.

Following the Koppers gasifier runs, a Karpely gas producer was operated - first with two sizes of coke, and then with Disco low-temperature char. The tests, conducted in cooperation with the American Gas Association and Kopper Co., Inc., were made with air and with 50, 75, and 98 percent oxygen-nitrogen mixtures. They proved quite successful and very informative.

A vertical coal gasifier of the Morgantown-type also has been installed and is being prepared for the first run.

Economic studies for commercial-scale plant operations continued. Considerable effort was devoted to the preparation of an estimate for a 10,000-barrel-a-day coal gasification and gas synthesis plant which, although not yet completed, is now being reviewed by a committee appointed by the National Petroleum Council.

Laboratories and Pilot Plants, Bruceton and Pittsburgh, Pa.

Research of the laboratory and pilot plant staff at Bruceton, Pa., was centered in 1950 on developing new or improved processes for producing liquid fuels from coal by (1) synthesis of its gasification products (Fischer-Tropsch and related processes); (2) direct high-pressure hydrogenation (Bergius process at 3,000 to 10,000 pounds per square inch); and (3) medium-pressure fluidized coal hydrogenation (about 1,000 p.s.i.).

In pilot-plant synthesis studies, internally-cooled reactors (cooled by oil circulation through a catalyst bed) were operated to determine the practicability of using fused-iron catalysts. To eliminate a catalyst cementation problem encountered in operations with a fixed bed of catalyst, a "moving-catalyst-bed" process was developed that offers such additional advantages as higher space-time yields, less catalyst required, lower operating temperatures, and greater ease of adding and withdrawing catalyst. Various process modifications, such as recycle-gas scrubbing for carbon dioxide removal and continuous removal of oxygenated compounds from the total off-gas, also were investigated.

The substitution of nitrogen for carbon in the crystal lattice of carbided iron synthetic-ammonia-type catalysts has been explored. A study of the effect of various structural promoters in these nitrided catalysts on activity and product distribution, has shown that relatively low methane plus ethane, low wax, and maximum gasoline production is possible. Studies also were made of the changes occurring in fused-iron catalysts during such treatments as reduction, oxidation, and nitriding. These studies have resulted in catalysts of greatly improved durability.

Process development and catalyst research were carried out in connection with the circulating slurry process, in which synthesis gas is bubbled through a suspension of finely powdered catalyst in a high-boiling oil.

In the course of a study of the mechanism of the Fischer-Tropsch synthesis some fundamental work was done on the OXO process, in which aldehydes and alcohols are produced from olefinic hydrocarbons and by a study of the primary oxygenated products obtained from iron catalysts.

Special analytical techniques combined with the application of known spectrometric and physical chemical procedures have been used in determining the constitution of products from the gas synthesis process.

The liquid-phase coal-hydrogenation pilot plant was operated to yield information on process variables, catalysts, and feedstocks. When hydrogenated at 1,500 p.s.i. with ammonium molybdate catalyst, coal from Rock Springs, Wyo., yielded a heavy fuel oil and a middle oil. Although this pressure is much lower than that normally used in coal hydrogenation, the process is operable.

The liquid-phase coal-hydrogenation plant was converted into a fixed-bed-catalyst unit for hydrogenating coker distillate from shale oil. At 1,500 p.s.i. using a cobalt molybdate catalyst, about 30 barrels of jet fuel and Diesel oil were produced.

The vapor-phase hydrogenation unit was operated to test the efficiencies of various catalysts, and a large number of batch autoclave experiments were carried out in the search for new catalysts and in the investigation of coal-hydrogenation reaction mechanisms. Process variations and design modifications were investigated in bench-scale units such as the fluidized-bed hydrogenation unit and the variable contact-time unit. Preliminary results indicate that fluidized-bed or dry-coal hydrogenation compares favorably with high-pressure liquid-phase hydrogenation and offers definite economic possibilities. Thus, this process is being developed on a pilot-plant scale.

A study is being made of the nature of the oxygen linkages present in coal. A comparison was made of the products obtained from the hydrogenation at 400°-450° C. of coal and those from a similar treatment of sugar, the former substance having a presumably aromatic structure and the latter, an aliphatic structure. The products from both substances were proved to be essentially the same.

In Pittsburgh, the gasification of coal with oxygen and steam was studied in an experimental unit of the vortex type using a specially designed coal distributor. Tests were made which resulted in modifications of the gasification unit design, and additional studies of the relation between reactor design and carbon conversion are being carried out.

<u>Synthesis-Gas Laboratory and Field Tests, Morgantown, W. Va., and Gorgas, Ala.</u>

At Morgantown, W. Va., pilot-plant experiments in the gasification of pulverized coal have helped to solve a number of problems standing in the way of producing at reasonable cost the synthesis gas required in making synthetic liquid fuels by the Fischer-Tropsch process. As synthesis gas now constitutes 60 to 70 percent of the final product cost, competitive synthetic fuels depend largely upon finding a way for obtaining this hydrogen-carbon monoxide mixture at lower cost. Coal gasification also is employed in producing the hydrogen used in the direct coal-hydrogenation process.

In this experimental program, done in cooperation with West Virginia University, several new processes are being created and evolved systematically, and data essential to the design of large-scale plants are being obtained. Experimental units at the Morgantown station include:

(1) A small-scale experimental plant for gasifying 50 pounds of pulverized coal per hour. Operated successfully for several years, this plant is believed to have been the first pulverized-coal gasification unit capable of continuous operation. Its operation supplied data required for the design of larger units. The plant has gasified successfully up to 35 pounds of dried, pulverized, subbituminous coal per cubic foot of generator volume per hour. About 85 percent of the carbon in the coal was gasified in a single pass.

(2) A larger-scale pilot plant for gasifying pulverized coal with extremely high-temperature steam and oxygen at pressures near atmospheric. More than 400 pounds of pulverized coal per hour has been gasified successfully in this plant, and synthesis gas of excellent quality produced. Steam has been heated to more than 3,500° F. - an unprecedented high temperature for the large volumes used. Overall plant performance, as measured by consumption of oxygen, steam, and coal per unit of synthesis gas produced, is very good.

(3) An experimental pilot plant is now in operation for studying the purification of synthesis gas, using organic solvents to remove the sulfur. Standards of purity required in the finished synthesis gas are so high that it was necessary to develop new methods for purification.

(4) Construction is 80 percent complete on an experimental pilot plant for gasifying pulverized coal in steam and oxygen under a pressure of 450 pounds per square inch. Preliminary cost studies have indicated that, if a plant of this type can be made to work, very considerable reductions in the cost of synthesis gas will be forthcoming. As planned, the ash will be removed as liquid slag from the generator. This plant also interests the chemical industries, for it appears especially promising for the production of synthesis gas for making ammonia and alcohol.

The process for gasifying pulverized coal, as developed at Morgantown, is flexible both in the control of hydrogen:carbon monoxide ratios and in the use of widely different coals. This flexibility makes the process applicable to a variety of uses in the synthesis field.

Recent work has demonstrated that suitable refractories for heating steam to 3,500° F. are available; that slag formed in the operation of the gasifier can be tapped continuously; and that a satisfactory dust-removal system can be made from standard equipment.

At Gorgas, Ala., the Alabama Power Co. and the Bureau of Mines have jointly operated for 20 months a field-scale experiment in gasifying coal underground. Gases produced by burning unmined coal under controlled conditions offer a possible low-cost fuel for generating electric power as well as materials for conversion to liquid fuels.

Two parallel entries were driven into a coal bed for 1,200 feet and a single entry for an additional 300 feet. At crosscuts linking these entries, the underground workings were connected with the surface by five large boreholes through which compressed air may be admitted or product gases withdrawn.

Operation was maintained in the section between boreholes I and II for 16 months, during which 5,900 tons of coal were consumed. An area of the coal bed varying between 100 and 150 feet in width was burned out. The total heat in the product gas reached a maximum for the eighth month of about 70 percent of the heating value of the coal consumed.

The section between borehole III and new borehole VII was operated for 4 months. Gas of appreciable calorific value was obtained for the first several weeks, but the gas quality declined as the coal near the boreholes was consumed. The rate of coal consumption at comparable air input rates was much greater in this section, and the heating value of the gas, expressed as percent of the coal's combustion heat, was higher.

A gas turbine installation was operated for a short period, using some of the energy of the hot product gas to provide additional air for the system.

By-passing of the hot carbon faces by unreacted air has been the chief difficulty encountered. Some success has been achieved in controlling by-passing by filling void space underground with fluidized sand.

Oil from Oil Shale

Experimental Mine, Rifle, Colo.

Again in 1950, improved methods and lower costs were demonstrated for mining the oil-rich Green River shale formation of the Rocky Mountain area, while estimates of potential reserves in northwestern Colorado once more were revised upward.

Based on information now available, it was estimated that Colorado's oil-shale beds alone would yield nearly 500 billion barrels if all of the oil were recoverable. Of this, 126 billion barrels would come from the richer Mahogany ledge. The oil shale extends well into Utah and Wyoming, but the formation in these states has not been as intensively explored.

Underground operations in the Experimental Oil-Shale Mine, on Naval Oil-Shale Reserve No. 1, near Rifle, Colo., were carried on during 1950 in two sets of workings - the Selective Mine and the Underground Quarry. The processing plant used shale mined from the Underground Quarry, and activities in the Selective Mine were limited to test room research. Shale broken and transported from the Underground Quarry during the year amounted to 58,500 tons.

Emphasis was placed on drilling and blasting research in the Underground Quarry. Percussion-drilling studies led to a one cent per ton reduction in operating costs, principally by increasing the life of drill rods through improvements in heat-treating procedures. Comparative tests of numerous types of percussion drill bits resulted in the selection of one which has drilled more than 1-1/2 miles in oil shale.

Rotary drilling experiments were conducted, using a rotary test drill developed at Rifle. This drill offers a wide range of operating conditions and is supplying data for use in designing an effective drill bit and in determining optimum operating characteristics.

Three types of blasting research were conducted. Instrumented blasting experiments were made in studying millisecond detonation, depth of destructive penetration, and amount of dynamic strain developed in rock at various distances from the explosive charge with different types of explosive and loading procedures. Individual blast hole experiments completed on the middle bench of the Underground Quarry provided data for selecting the best type of explosive and blast-hole diameter.

A new series of blasting experiments is under way involving the application of statistical engineering both in designing the procedures and analyzing the data. They show promise of greatly reducing the number of experiments necessary to obtain a given amount of information.

Investigations of stresses in mine structures yielded data useful in determining safe room spans and pillar dimensions. A study of Diesel exhaust gas scrubbers resulted in the design of a unit capable of removing as much as 85 percent of the aldehyde content of exhaust gases from a 150-hp. Diesel engine.

Production mining equipment used in the Underground Quarry was designed and built in 1948 and 1949 and has been described previously. Three new units of auxiliary equipment were added in 1950, however. These included: (1) An acceptable Diesel-powered conveyance for transporting explosives to the underground working places; (2) a Diesel-powered water truck, equipped with a 1,300-gallon flat-bedded tank and a 50-gallon-per-minute pump, for wetting down piles of broken shale before loading, sprinkling haulageways, transporting water to a portable utility station, and pumping water from underground sumps; and (3) a portable electric substation which provides switching equipment, low voltage and overload protection, and transformer facilities at remote locations in the mine.

A new cost estimate was made in 1950 for commercial-scale mining of the Mahogany ledge of the Green River formation. This estimate was based on mining 19,200 tons of oil shale daily at one of a number of possible sites in the Rifle-DeBeque area of western Colorado. The mine site would be 1.4 square miles in area and would supply for 20 years the raw material requirements of a processing plant producing 11,700 barrels of shale oil daily.

Total capital expenditure for the mine was estimated at $4,750,000, and it is believed that full production could be achieved in 18 months. The estimated cost of mining, crushing, and conveying the shale to the retort stockpile was 42.6 cents per ton. This figure included management, depreciation, taxes, and insurance, but did not provide for depletion, interest on investment, profit, nor expenditures for off-site facilities.

Demonstration Plant, Rifle, Colo.

An oil-shale industry was brought closer to reality in 1950 when a new and promising process for continuous extraction of oil from shale was demonstrated in a pilot plant at the Bureau's Oil-Shale Demonstration Plant near Rifle, Colo.

The new development, called the "gas-combustion retort," gets its name from the distinguishing feature of the process - combustion of a low B.t.u. gas to provide the heat for retorting. The combustible components - carbon monoxide, hydrogen, and gaseous hydrocarbons - are evolved from the shale during retorting.

Another important feature is that no water or air cooling is required, for all heat exchange takes place between gas and shale within the retort. The fact that no water is required is a distinct advantage, for water is a scarce and valuable commodity in the semiarid region of Colorado, Utah, and Wyoming, where the nation's major oil-shale reserves exist.

Most important of all, investment and product costs for the new process will be substantially lower, according to a recent cost estimate, than for other retorts such as the "gas flow" on which previous cost estimates were based.

Crushed raw oil shale is fed into the top of the vertical retort and moves downward by gravity against a rising stream of gas. Near the center of the vessel, air is injected and the gas burned to provide heat for retorting. As the rising gas from the combustion zone and the downward-moving shale pass each other, the shale is heated and the gas is cooled. Upon leaving the retort, the gas passes through an oil-recovery system. Part of it is returned to the bottom of this retort where it is preheated by spent shale before entering the combustion zone. The remainder, or excess, could be burned to generate heat and power.

Another highlight of the year's activities was a demonstration in which, for the first time in America, a railroad train was powered by shale-oil Diesel fuel. The fuel was manufactured in the Bureau's demonstration shale-oil refinery and was burned in the Diesel locomotives of the "Prospector," a passenger train of the Denver and Rio Grande Western Railroad, during its regular trip from Salt Lake City, Utah, to Denver, Colo., on September 1.

Experimental operation of the gas-flow retort has been continued, and a valuable fund of engineering knowledge has been accumulated that can be used in projecting this retort to a larger scale or applied to the design of other types of retorts.

Refining operations have demonstrated that gasoline meeting regular-grade specifications and a good grade of Diesel fuel can be produced by coking and other thermal cracking processes, followed by acid treating, rerunning, and sweetening. Tetraethyl lead blending equipment is being installed so that finished gasoline can be produced for road tests. Shale Diesel fuel has been used continuously in trucks and other Diesel equipment on the project for more than six months. Performance has been excellent.

For a shale-oil industry of any significant magnitude, say 100,000 barrels a day or more, it might be advantageous to pipe the oil to the area in which most of the finished products are to be marketed before refining it. Accordingly, studies have been made to determine how the pour point and viscosity of crude shale oil might be lowered enough to yield a suitable stock for pipeline transportation. Either viscosity-breaking or coking, as demonstrated by refinery operations at Rifle, would produce a synthetic crude oil that could be piped to a marketing area such as the west coast or Chicago.

Twenty cooperative agreements have been added to those that were in effect with industry and universities at the beginning of 1950. These agreements are of two types. Under one, the Bureau of Mines supplies oil shale, shale oil, and shale-oil products to cooperators for experimental work in exchange for the results of their experiments. In the other, the cooperator supplies equipment to the Bureau for testing to determine what application the equipment may find in an oil-shale industry and in return he receives the results of the tests.

A cost estimate for the production of gasoline and fuel oil from oil shale was prepared from preliminary data available on the gas-combustion retorting process and from recycle cracking and acid treating tests in the demonstration refinery. A plant was designed to consume the output of an oil-shale mine of the most efficient size, using the mining method developed and demonstrated at Rifle. This estimate indicates a pay-out time for the construction investment, before income taxes and general overhead expenses, of between 5 and 9 years, if gasoline values equivalent to posted tank-car prices at nearby refineries in the Wyoming-Utah area are assumed.

Laboratories and Pilot Plants, Laramie, Wyo.

At year's end, intensive development work was under way in the Oil-Shale Experiment Station at Laramie, Wyo., on a shale retorting process that appeared particularly promising in view of current shortages and increasing requirements for strategic chemicals and high-octane blending stocks.

A pilot plant rapidly was taking form on the drafting boards after bench-scale experiments disclosed that a highly aromatic oil is produced when pulverized oil shale is retorted almost instantaneously at high temperatures (1,500° F.). This crude oil contained 15.5 volume percent of benzene, required in manufacturing synthetic rubber, plastics, nylon, and insecticides.

The unleaded gasoline fraction from the crude oil had an A.S.T.M. motor method octane number of 98 and contained 58.4 percent benzene, 24.5 percent toluene, and other higher aromatics. Hydrocarbon constituents of the gas produced in the process were largely ethylene, hydrogen, and methane, together with smaller quantities of propylene, ethane, butylenes, and butadiene.

Retorting research in 1950 was directed toward establishing the effects of temperature and heating time on the quality and quantity of gaseous and liquid products formed from oil shale, and the effects of these variables on the decomposition of mineral carbonates in the shale. Results indicated an optimum retention time at each specific temperature from 850° to 1,100° F., above and below which the yield of liquid products decreases. Higher temperatures and shorter retention times favor maximum liquid production. Over the range of conditions studied, it appeared that the quality of the oil was a function of the extent of cracking in the retort, and that variations in retorting temperature and retention time had an effect only on the extent and not on the fundamental nature of the conversion reactions.

Refining research included studies of catalytic cracking, hydrogenation of crude shale oil and coker distillate, catalytic reforming of hydrogenated and thermally-cracked naphthas, solvent extraction of distillates, and composition of thermally-cracked naphthas.

Hydrogenation of about 40 barrels of coker distillate from crude shale oil at pressures under 1,500 p.s.i. reduced the sulfur and nitrogen contents and yielded Diesel and jet fuels that meet military specifications with minor additive blending. Reforming would be necessary to produce satisfactory gasolines. Hydrogenation of crude shale oil under similar conditions was not entirely satisfactory because of coke deposition and insufficient removal of nitrogen. A search for better catalysts is being made.

Solvent extraction of shale-oil gas oil using furfural and some other solvents also produced good quality Diesel fuels and catalytic cracking stocks with low sulfur and nitrogen contents and low carbon residues. Catalytic treating of thermally-cracked naphthas over bauxite or similar catalysts reduced their nitrogen and sulfur contents and improved their octane rating and tetraethyl lead susceptibilities.

More than 3,000 additional assays were made of oil shale samples, principally from core and oil-well drilling operations in the Green River formation, and full chemical analyses were completed on shales from each of the distinctive beds in the Experimental Oil-Shale Mine at Rifle, Colo.

Research on shale-oil composition was emphasized in 1950, with studies including comprehensive analyses of high-temperature retort oils, naphthas from recycle thermal cracking of gas oil, and the separation and identification of the nitrogen, sulfur, and oxygen compounds that cause many of the problems in shale-oil processing.

Research on methods for analyzing shale oils and their products resulted in the development and publication of two applications of selective adsorption techniques and of a comparison of the bromine number, nitrogen tetroxide, and silica-gel methods for determining olefins in naphthas. Reliable methods were developed for determining nitrogen in samples containing refractory nitrogen compounds and for titrating basic nitrogen compounds.

The yields and properties of waxes extracted from shale-oil wax distillate were determined and the results published. Shale-oil waxes meeting specification requirements for commercial paraffin wax were made.

Tar acids and tar bases, byproduct materials from shale-oil refining operations, were separated and purified to determine the quantity and quality of these products available. Results indicated that commercial quality products can be made in sufficient quantity to affect favorably the economics of oil-shale processing.

Preliminary tests also showed that topped shale oil can be reduced by air blowing to asphaltic residuums of suitable penetration consistency.

Liquid Fuels from Agricultural Residues

Semiworks Plants, Peoria, Ill.

From appropriations authorized by the Synthetic Liquid Fuels Act, the United States Department of the Interior transferred, for fiscal years 1949 to 1950, inclusive, $510,000 to the United States Department of Agriculture for research and development on the production of alcohol and other liquid fuels from such agricultural residues as corncobs and the hulls of cottonseed, oats, and rice. With these funds, the Bureau of Agricultural and Industrial Chemistry constructed and equipped a small industrial plant at Peoria, Ill., and started operations to determine the manufacturing steps and costs of a process of its own development. These operations were terminated at the end of the fiscal year 1950 due to lack of funds.

The Liquid Fuels Plant was located on the site of the Northern Regional Research Laboratory at Peoria to permit coordination of the programs of the two groups and more rapid evaluation of the possibilities of the process. The Northern Regional Research Laboratory is studying the kinetics of conversion of the xylose in the pentosan hydrolyzates to furfural and the fermentation of the pentose and dextrose sugars to liquid fuels.

Basically, the hydrolysis process investigated consists of converting one of the fractions of agricultural residues - pentosans - to pentose sugars and subsequently converting the cellulose fraction to dextrose. The pentose sugars may be fermented to the liquid fuels butanol, isopropanol, acetone, and ethanol or they may be converted to furfural. Dextrose, on the other hand, may be converted to the liquid fuel ethanol. The fundamental economic advantage of this particular process is that pentose sugars and dextrose can be separated almost quantitatively; therefore, each one in its turn can be converted to maximum yields of end products.

At the time operation of the semiworks plant was terminated, the study of the hydrolyzation process as originally outlined had been completed. Every single operational step for the degradation of the pentosans to xylose and the cellulose to glucose on a semiworks scale had been perfected to such an extent that the plant was operating continuously under routine conditions at an hourly capacity of 550 pounds of cobs. The final products obtained from this operation were two types of hydrolyzates, one containing chiefly xylose from the pentosans, the other glucose from the cellulose, and, as residue, lignin, combined with remnants of polysaccharides which remain unhydrolyzed.

From the routine operation of the process, a sufficient amount of production data was assembled to permit an accurate evaluation of the performance of each operational step and of the entire process. Based on these data, a material balance diagram for both phases of the process was prepared. This diagram revealed that under the present operating conditions, 1 ton of air-dry corncobs yields 452 pounds of xylose in the pentosan hydrolyzate, 205 pounds of glucose mixed with 94 pounds of xylose in the cellulose hydrolyzate, and 429 pounds of residue. Certain major alterations of the present process and procedure are strongly recommended in order to increase the over-all efficiency.

With these alterations, it is estimated that xylose can be produced at a price slightly below 2 cents a pound which is competitive with the sugars in blackstrap molasses at a price above 12 cents per gallon.

Studies on the kinetics of the conversion of xylose in pentosan hydrolyzate led to the development of a conversion process on a laboratory scale. With this process, furfural yields of 65-66 percent of the theoretical were obtained.

A series of large-scale fermentations with pentosan hydrolyzate and cornmeal as substrate in 3,000-gallon pilot-plant runs was made in order to study the production of butanol, acetone, and ethanol. These runs were conducted with a fermentation efficiency of 80-85 percent. A fermentation period of 96 hours was required.

Secondary Recovery and Refining Research

Through an amendment to the first Synthetic Liquid Fuels Extension Act, funds were made available on July 2, 1948, to conduct research on secondary recovery from stripper oil fields and on refining problems. Results of the first 18 months work were presented in the 1948 and 1949 Annual Reports. Since June 30, 1950, this research has been financed from other appropriations; hence, the current report is confined to operations during the first half of 1950.

Engineering field studies of secondary-recovery operations were conducted in the Mid-Continent, Texas, California, and Appalachian regions. Information on the production histories and the reservoir conditions of representative stripper fields was collected, analyzed, and published, enabling other producers to ascertain and apply the stimulative methods that have proved most efficient in producing oil under given conditions.

Significant advances were made in fundamental research on the nature of the forces that hold crude petroleum in the underground reservoir rocks: (1) A new method was developed for measuring precisely the permeability of packed beds of sands and powders of flowing liquids; (2) devices were under construction for accurately measuring streaming potentials, gas absorption, and interfacial tensions of systems containing surface-active constituents; and (3) surface-active and film-forming substances were extracted from crude petroleum of two fields.

Although concerned with numerous individual problems, the engineering research on secondary recovery uniformly was directed toward obtaining more oil from stripper fields by scientifically planned and engineered methods of stimulation. Problems encountered in shooting oil and gas wells with explosives, for example, were under attack on two fronts: (1) Through research on explosives and their blast effects; and (2) through a survey of the physical properties of oil-bearing rocks from representative fields, which was made possible by the provision of drill cores by many interested oil and gas companies. Other projects and investigations included selective plugging of air-injection wells; studies of earth temperatures, reservoir oil samples, and pore patterns; ways by which oil wells may be made to flow on gas-injection projects; cable-tool coring with improved drilling fluids; means of locating abandoned wells; and studies of both water conditioning for subsurface injection and of the effects of dissolved gases on corrosion of metal by water. Meanwhile, work began on the use of radio-active tracers for water injected into oil sands during flooding operations. The effect of heat on oil recovery also was explored.

Special techniques and laboratory analyses, of course, were an indispensable part of this secondary-recovery research. Points of major emphasis were core and water analyses, electrical logging in shallow fields to find the upper and lower limits of oil-bearing formations, and the provision of special tools. An acutely needed small-diameter well caliper was developed and now is being shop tested in preparation for early field tests.

The major objective of the petroleum chemistry and refining program has been to improve the usefulness of the marginal crude oils, particularly those having high sulfur contents. Material progress was made in 1950 toward determining the characteristics of sulfur-bearing distillates from selected crude oils.

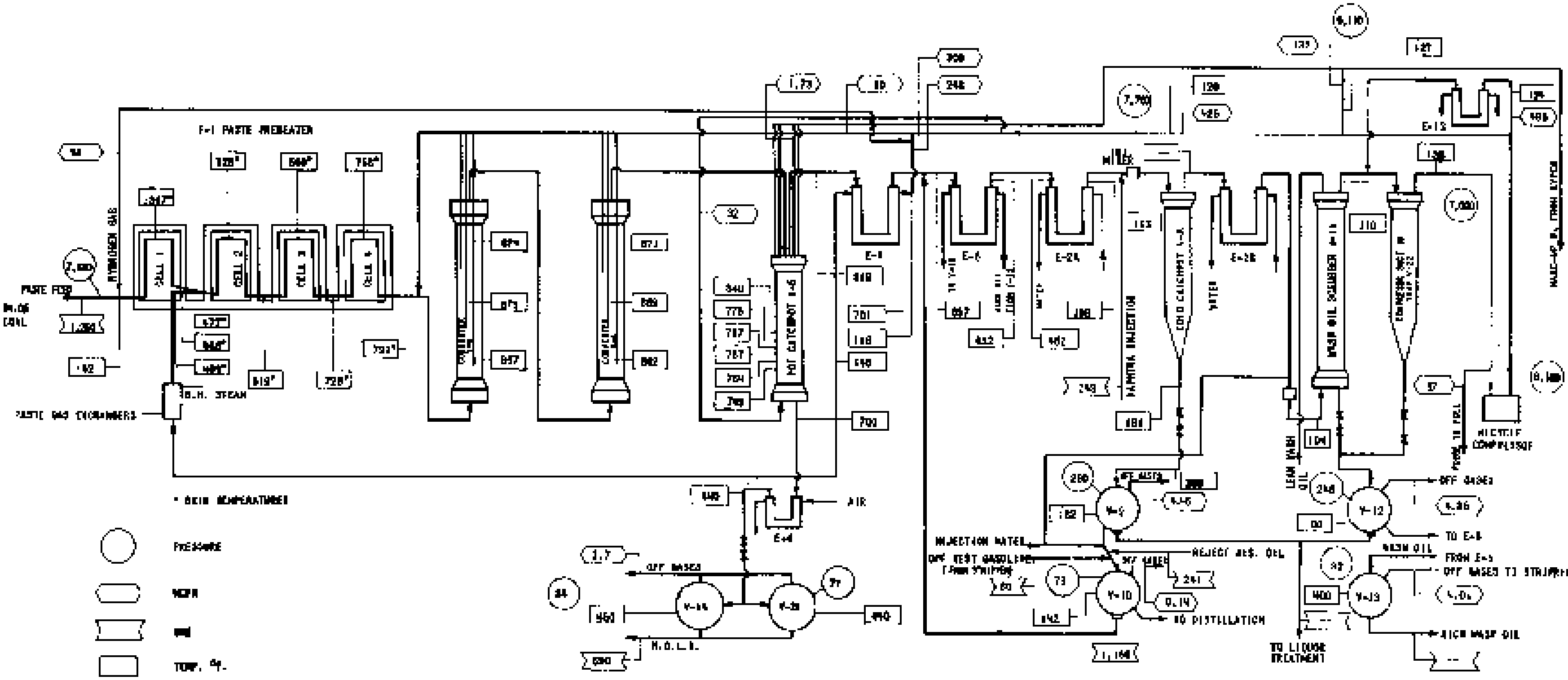

Figure 2. - Liquid-phase hydrogenation unit - typical operating conditions - Rock Springs coal hydrogenation.