INTRODUCTION

For the past ten years, under the authorization of the Synthetic Liquid Fuels Act of April 1944 (30 U.S.C. Secs. 321-325 and ammendments), the Bureau of Mines has carried on an extensive research and development program to establish methods for the production of oil from coal and oil from shale.

This law originally was passed by the 78th Congress under the stress of wartime demands for liquid fuels to supply our armed forces. It was extended when peacetime demands for oil and oil products surpassed peak requirements of World War II.

Although the demand for liquid fuels seemed to level off in 1946, it has since increased steadily to a new peak in 1953. Figure 2 shows that, in the short span of one decade (1943 to 1953), consumption of liquid fuels has nearly doubled, increasing from about 1.7 billion barrels per year in 1943 to nearly 3 billion barrels per year in 1953.

Since World War II supply has kept pace with ever-increasing demand, but only through imports of more and more oil. These imports approached one-half billion barrels of oil in 1953. Most of the increased use has been in the field of motor and other distillate fuels which probably will be used in still greater quantities in the immediate future. An estimate of this demand and how it will be met was made by Ayres (fig. 3).

According to his predictions, imported oil will continue to meet the demand for distillate fuels for some time. However, he expects shale oil to begin to make up the difference between production and demand as early as 1957.

Other authors have different opinions as to when synthetic liquid fuels will come into the market, but all agree that this time will come eventually, probably within the next decade.

In its research and development program on synthetic liquid fuels, the Bureau of Mines is obtaining engineering and cost data for the day when industry will require such figures and has increased its more basic research work during the past year to learn more about the nature of the raw materials and their suitability for new processes to convert both coal and shale to oil.

To accomplish this purpose, the Bureau of Mines has built and operated three laboratories and two engineering plants. The first laboratory was erected at Laramie, Wyo., and is dedicated to the study of oil shale and related problems; the second laboratory was constructed at Bruceton, Pa., and deals with the broad problem of coal-to-oil processing. More recently a new laboratory, which is concerned with the conversion of coal to gas, both for direct use as fuel and for synthesis of liquid fuels and chemicals, has been completed and occupied at Morgantown, W. Va.

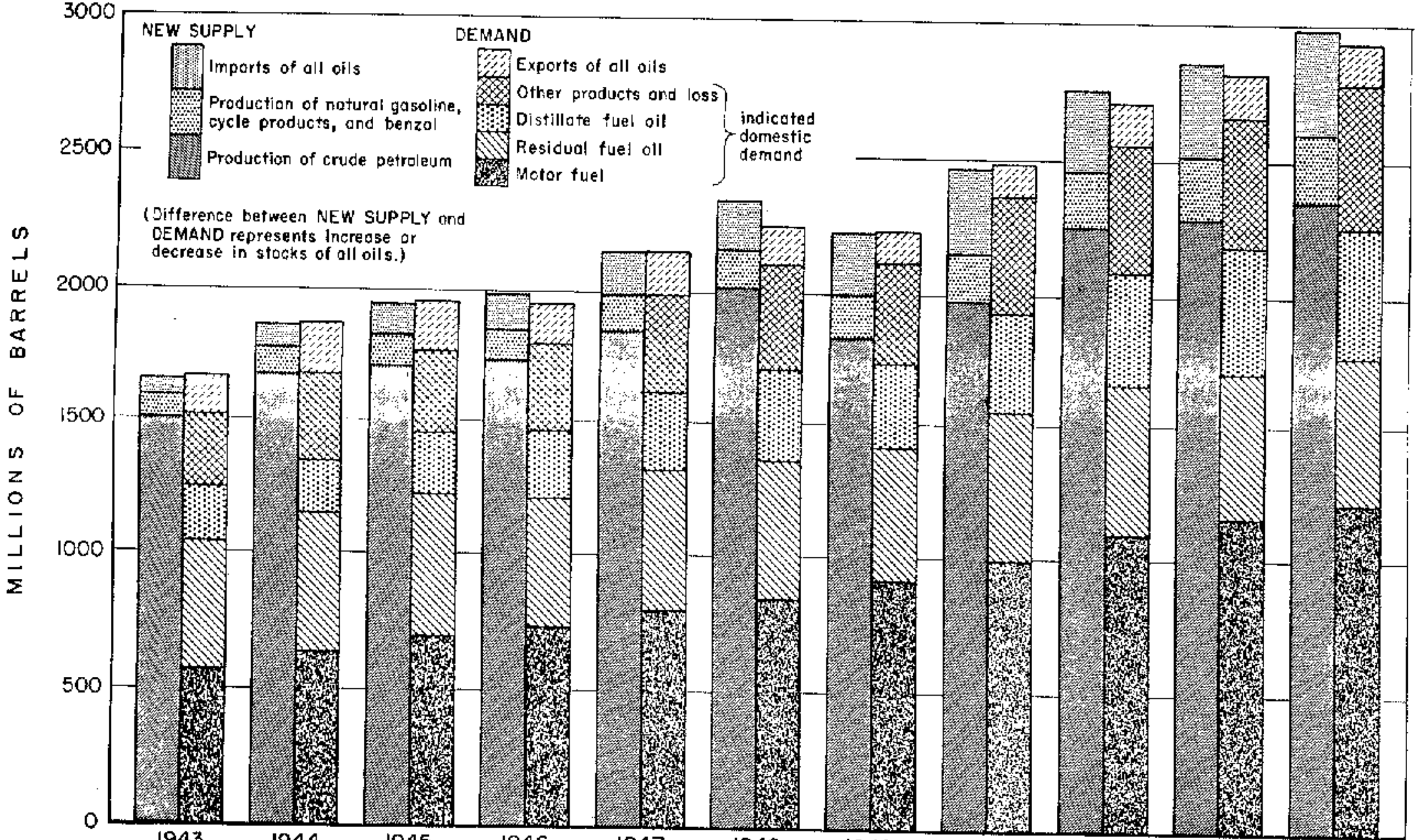

Figure 2. - Supply and demand of all oils in the United States, 1943-53 (preprint from Bureau of Mines Minerals Yearbook for 1953).

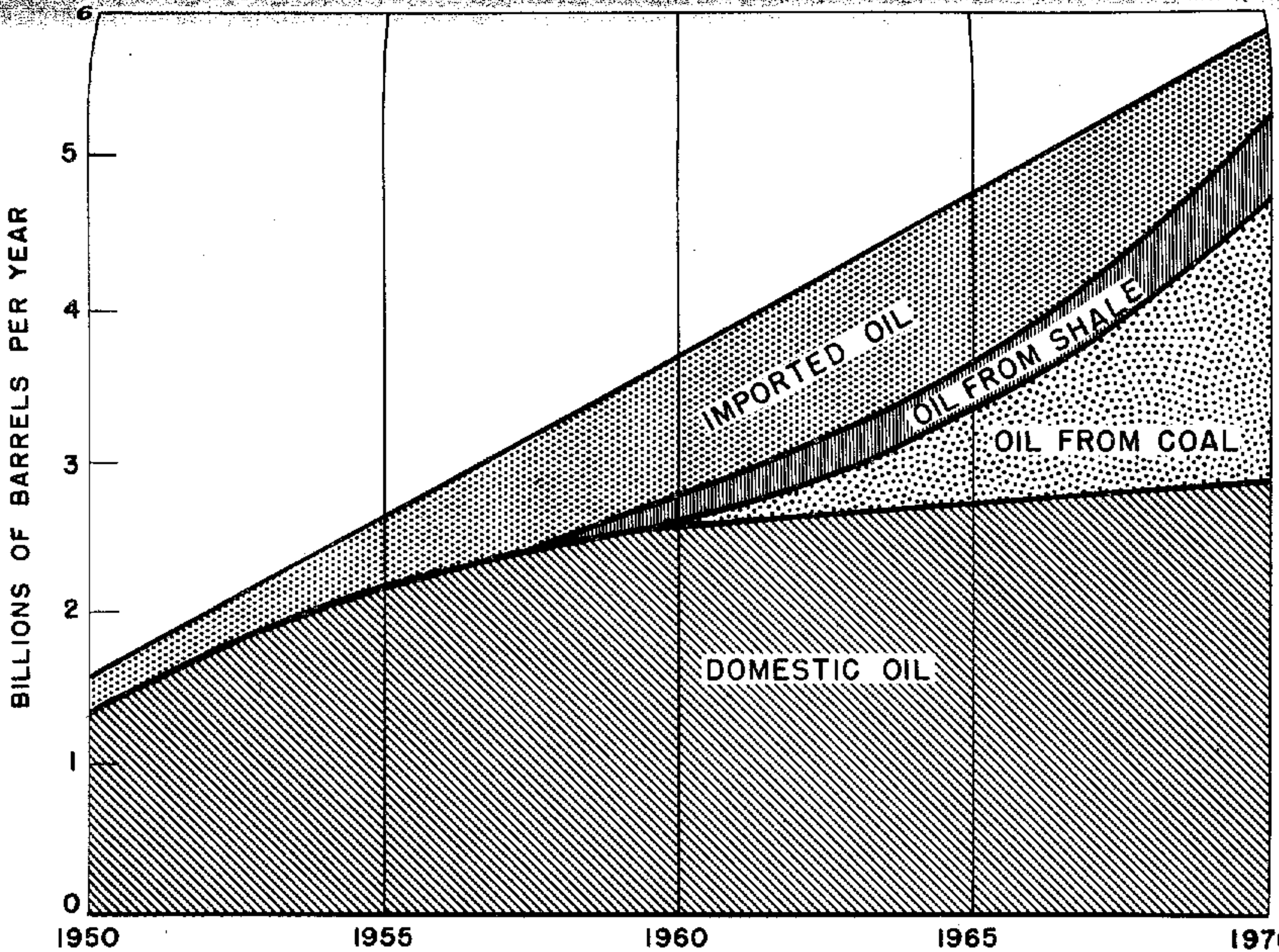

Figure 3. - Future sources of distillate fuels (Ayres, E., Coal Age, August 1953, p. 70).

An experiment station at Rifle, Colo., was built to demonstrate methods for mining and retorting oil shale and for converting crude shale oil to other fuels by refining. A station at Louisiana, Mo., was used to demonstrate on a semi-commercial scale the conversion of coal to oil by direct hydrogenation and the conversion of synthesis gas (made from coal) to liquid products by means of the Fischer-Tropsch process. This station was closed in June 1953 and turned back to the army for disposal.

Besides the installations mentioned, at Gorgas, Ala., on property of the Alabama Power Co., a joint investigation has been conducted on the gasification of coal underground. This project was scheduled to end in July, 1954, but it has been reactivated with the help of the Alabama Power Co. and the Stanolind Oil and Gas Co. to investigate a promising method of underground fracturing.

Enumeration of the physical facilities gives some idea of the scope of the Bureau's program on synthetic liquid fuels. Summaries of the year's accomplishments at each of the operating stations are given in the sections that follow.

Summary of 1954 Operations

Oil From Coal

Laboratories and Pilot Plants, Bruceton, Pa.

At laboratories and pilot plants in Bruceton, Pa., research was continued on producing synthetic fuels from coal by gas synthesis and hydrogenation. The structure of coal has been studied to obtain fundamental data on its behavior in chemical processes. Analytical methods were developed for process control and product characterization.

Longevity tests were made on steel turnings which are excellent catalysts for the Fischer-Tropsch oil-circulation process. After long periods of synthesis, changes in composition of the products indicated that the catalyst had become deficient in alkali. The quality of the catalyst was restored, however, by injecting an alcoholic solution of potassium hydroxide into the reactor. The active surface layer was found to be largely converted to Hägg iron carbide early in the synthesis. The carbide content then remained essentially constant, but metallic iron was slowly oxidized to magnetite.

Small-scale experiments were made to develop improved methods of activating and pretreating iron turnings and steel wool. At 800° C. the turnings were completely oxidized in a relatively short time. At 600° C. oxidation was rapid initially but became very slow after about 20 percent of the iron had been oxidized. Turnings that were carbided or nitrided before synthesis had relatively low activity, but subsequent oxidation and reduction of the catalysts resulted in high activity. Activated turnings of a variety of steels had about the same activity. However, higher activity was observed with a steel containing copper and with oxidized turnings of carbon-steel impregnated with copper nitrate. Oxidized steel wool also was very active in the synthesis. Available data indicate that the activity of steel turnings increases approximately linearly with surface area.

Borides of iron have structures similar to carbides of iron. Experiments are being made to produce borided catalysts by treating iron with diborane.

The Fischer-Tropsch slurry process was studied in bench-scale units designed to maintain a high velocity of oil-catalyst slurry to minimize agglomeration of particles. This troublesome phenomenon is probably associated with the complex colloidal nature of the slurry. Higher alcohols added to the oil decreased the tendency toward separation. A method was developed for reducing finely divided catalysts in a dry, fixed-bed reactor before slurrying the catalyst with oil.

Studies were made in pilot-plant equipment of the process for removing carbon dioxide from synthesis gas by means of a hot, concentrated solution of potassium carbonate. They confirmed earlier results obtained in smaller apparatus, showing that substantial savings in steam and capital investment can be achieved as compared with conventional methods.

Hydrocarbonyls of iron and cobalt have chemical properties and structures that appear to be similar in many respects to those of intermediates postulated for the Fischer-Tropsch synthesis. To gain further insight into the mechanism of the synthesis, the structure and reactions of such hydrocarbonyls have been studied.

Hydrogenation of coal to liquid fuel at high temperatures, a departure from the conventional method as only one step is required instead of two, has been studied in continuous reactors rather than batch-type operation. Rock Springs (Wyo.) coal, impregnated with ammonium molybdate, was used with a volatile vehicle oil. Bench-scale studies at 525° C. of rates of flow of gas and coal paste showed that they caused only small differences in conversion and product distribution. Sizable quantities of heavy oil and relatively small yields of gasoline and gaseous hydrocarbons were produced. Conversion of coal to oil was nearly complete, and the oils contained only 1 to 2 percent of asphaltenes.

Similar products were obtained in a pilot plant where a variety of difficulties due to overheating were encountered. The plant was operated with moderate success at temperatures as high as 510° C. On the basis of these experiments, the reactor was redesigned. The present system employs a paste preheater followed by an adiabatic reactor that will be cooled by recycling hydrogen.

Research on the structure and chemistry of coal, supported by both Bureau of Mines and cooperative funds, included heating of carbohydrates, cellulose, and lignin (with or without hydrogen) or treatment with sulfuric or phosphoric acid to produce coallike chars. Polymerization reactions leading to the formation of these chars require the presence of a carbonyl group in the molecule. The coallike char and its precursors can be hydrogenated in the presence of tin chloride to products typical of coal hydrogenation.

Infrared absorption spectra of anthraxylon from bituminous coal, asphaltene from coal hydrogenation, petroleum asphalt, and gilsonite were found to be similar. Infrared spectra also were used to follow structural changes during carbonization of coal. Examination of coal by conventional and small-angle X-ray diffraction indicated the presence of crystalline structures about 14 Å in diameter. To obtain information on factors that influence the solubility of coal, the characteristics of several polycyclic molecules were determined in a series of solvents. Research was begun on microbial degradation of coal and related substances. These studies may add to the understanding of the structure of coal and lead to different methods for converting coal to more useful substances. Kinetic studies of the reactions of carbon with carbon dioxide and steam will provide data regarding reaction mechanism and reactivity of different types of carbon.

Continued development of analytical methods was necessary to meet requirements of the research program. A platinum spiral heated to 800° to 1,000° C. converted organic sulfur compounds quantitatively to hydrogen sulfide. Methods were developed for analyzing mixtures of alcohols or phenols by formation of trimethylsilyl ethers and subsequent testing by mass spectrometer. Structural-group analysis has been studied with a view to applying it to evaluation of high-molecular-weight oils.

Mass spectra of alcohols and ketones have been determined, and analysis of simple mixtures is now possible.

Synthesis Gas from Coal Pilot Plants, Morgantown, W. Va.

Acceptance by a prominent chemical manufacturer of a commercial-scale coal gasifier, operating at atmospheric pressure and based on developments made at the Morgantown Station, has coincided with conclusion of experimental work on this type of gasifier. The development program ended with a factorial experiment that evaluated more fully the effects of variables in the process.

Development of the high-pressure gasifier is continuing, and it appears that, when this process is brought to the same point of commercial acceptance, it will have even wider possibilities than the atmospheric process. A factorial experiment with this gasifier has indicated a need for further mechanical improvements, and these changes are being made as equipment is reerected in the new Morgantown Experiment Station building. When operations are resumed, the statistical method again will be used to determine more precisely the effects of variables that control the process. Similar design improvements are being made in the experimental coal feeding units, oxygen plant, and coal preparation facilities as they are installed in the new quarters in preparation for further tests.

Gas-purification work at Morgantown included further improvement of the dry dispersion method for determining the particle size of dust and development of a method using millipore filters for determining the size of particles or agglomerates as they actually exist in a gas stream. Bench-scale development work has been started on a counter-flow dust feeder that will be used for testing dust-removal equipment. Reproducibilities average about 5 percent except at very low dust concentrations.

In cooperation with General American Transportation Corp., pilot-plant studies were initiated to study the effectiveness of a gas-liquid contactor of turbomixer type for removing carbon dioxide and hydrogen sulfide from raw synthesis gas. As absorption of carbon dioxide and hydrogen sulfide is controlled almost entirely by liquid-film resistance, it is believed that agitation of aqueous solutions of diethanolamine, resulting in a spray of fine liquid droplets, would not only increase the rate of mass transfer but also result in a greater pick-up of carbon dioxide per volume of diethanolamine circulated.

Bench-scale research was done on the preparation of micronized coal suspended in steam for gasification with oxygen. Coal-water slurries were flashed to steam in heated metallic coils, causing size reduction (micronization) of the coal.

Rates of steam-carbon reaction were studied in a specially developed, electrically heated, isothermal reactor. A few grams of finely powdered fuel were charged at a constant rate and reacted with excess steam, with or without inert gases or oxygens. These studies proved that the differential timing technique is a useful method for determining reaction rates at various temperatures. A preliminary study has been completed on the effects of small concentrations of oxygen, and the effects of particle-size now are being investigated.

Exploratory research was begun on the selective sorption and recovery of oxygen from air. A small glass apparatus and a bench-scale metallic apparatus have been constructed. Both are being used for fundamental sorption studies of various metal chelates and other chemical type oxygen carriers. Results obtained are correlated with simultaneous polarographic studies of the same sorbents.

Layouts were made for all equipment in the Morgantown Experiment Station. A contract was drawn up for moving and reerecting the principal pieces of equipment and their utilities. At present, the reerection of all facilities is approximately 90 percent complete.

A preliminary investigation has been started on the possibility of using heat from nuclear sources to promote the steam-carbon reaction.

Testing and improvement of component parts of the high-ratio centrifugal compressor is continuing.

Underground Gasification Project, Gorgas, Ala.

Since 1946, the Bureau of Mines and the Alabama Power Co. together have conducted a series of field-scale experiments on the underground gasification of coal. The first two experiments used mined passages within the coal bed. Operations showed that the cross-sectional areas of these passages were too large to maintain good contact between the gasmaking fluids and coal bed, which led to a gaseous product of poor quality even though a usable product was obtained at times.

A group of experiments was conducted next, using a process known as electrolinking-carbonization to prepare a passage in the coal bed. This process, originally developed by the Sinclair Coal Co. and the Missouri School of Mines, was adapted to the work at Gorgas. Three satisfactory passages were made by this method and, during operations, products of good quality were obtained. The method appears to be well adapted to underground gasification work; nevertheless, additional procedures for preparing passages in the coal bed are desirable.

In June 1954, cooperative agreements signed by the Bureau of Mines, Alabama Power Co., Stanolind Oil and Gas Co., and Halliburton Oil Well Cementing Co. provided for a joint investigation applying a hydraulic process for fracturing the coal bed. A process of this type, known as Hydrafrac, had been developed by the Stanolind Oil and Gas Co. to increase the productivity of oil wells.

A site was chosen at Gorgas 370 feet west of the old gasification workings and an injection well prepared. This well was cased with steel pipe to a point 12 inches within the coal bed, the casing cemented, and a 7-inch depth of coal exposed for treatment below the casing. The Hydrafrac treatment was applied by pumping into the well, in turn, 500 gallons of kerosene, 9,550 gallons of a viscous residual fuel oil to which 15,000 pounds of Ottowa flint shot sand had been added, and then 4,040 more gallons of kerosene. The heavy oil-sand was injected in 22-1/2 minutes at a flow rate of 425 gallons per minute and pressures ranging from 700 to 900 p.s.i. at the pumps. The follow-up kerosene was pumped at a rate of 185 g.p.m. over a 24-minute period.

Permeability tests using compressed air were made before and after the Hydrafrac treatment at the injection well. These indicated an 85-fold increase in permeability of the coal bed. At an injection pressure of 65 p.s.i., this represents an increase in air-injection rate from 6 to 520 s.c.f.m.

The extent and horizon over which the coal was fractured have not yet been completely determined. Test holes drilled on the line of the face cleats, 150 and 200 feet in opposite directions from the injection well, show the fracture to be in the coal bed. Oil, kerosene, and an air flow were found only at the horizon of the coal. An air flow and odor of kerosene vapor were noted at the outlets from the old gasification workings, indicating the fracture had extended some 370 feet in this direction. There is a possibility that the fracture extended 670 feet in another direction, intersecting an abandoned mine in the America coal bed. No signs of the fracture have yet been found at the coal outcrop whose nearest point is 850 feet from the injection well. However, tests completed to date indicate that a large area of coal bed has been fractured by the process.

It is planned to evaluate the extent of the fracture more thoroughly and then to ignite and gasify at least a portion of the treated coal bed.

Oil from Oil Shale

Oil-Shale Mining Branch, Rifle, Colo.

The mining program at the oil-shale mine comprises both research and production activities.

A lower adit driven to develop the bench level opened the full 73-foot height of the Mahogany ledge. Shale mined from either the 39-foot top heading or the 34-foot bench is of the same grade, eliminating the need for blending. One section of the mine road was timber cribbed to abate sloughing and subsidence. The main power substation was relocated, and new electric and blasting circuits were installed in the mine.

Collection, assaying, and logging of samples from the Green River formation were continued. Samples from 30,328 feet of drilling were collected from 26 core drill holes and 7 oil and gas wells in Colorado and Utah. A meeting with oil company representatives was held to standardize the terminology and methods for estimating reserves.

Research on rotary drilling included the use of statistical methods for testing rotary drill bits. The data were used in designing a rotary-drill heading jumbo now under construction. Cost estimates for commercial mining and paper studies of mining systems were prepared.

Oil-Shale Engineering Branch, Rifle, Colo.

Most significant of the changes made to the 6-ton-a-day gas-combustion plant was replacement of the original refractory-lined retort with an insulated stainless steel vessel. This alteration reduced heat losses and improved the flow of shale. Certain modifications in the oil-recovery equipment improved recovery efficiency and facilitated oil measurements. Effects of the changes were evaluated in a series of standard tests.

Secondary cracking of oil during retorting was studied. By secondary cracking is meant pyrolysis of oil in the retort under certain conditions after oil has been formed. Secondary cracking, if uncontrolled, is undesirable both in operability of the process and oil yield. A number of crude oils, representing different degrees of secondary cracking, were produced in the 6-ton-a-day retort, and selected ones were analyzed to determine which methods, if any, can be used to measure the degree of cracking. As part of the same study, a series of tests was made to (1) show the effect of rate of recycle gas upon secondary cracking and (2) investigate the effect of adding condensation nuclei. For the latter tests, sodium chloride was added in water solution to raw shale.

Construction of a 25-ton-a-day gas-combustion retort was completed. A number of exploratory operations were conducted in this plant.

A study of briquetting shale fines (minus 1/4-inch material) was initiated to develop means of retorting such fines which are now discarded. Briquets were produced with and without additives, but retorting of such briquets has not been started.

Several operations were conducted in the 150- to 300-ton-a-day gas-combustion plant to complete the shakedown and personnel training program. Approximately 41 operating days were required for this work. Following the shakedown runs, the plant was in operation for 59 days (on stream 94 percent of the time) without serious difficulties. Current studies are directed toward improvement of oil yield at reasonably high rates of shale throughput.

During shakedown operations, a study of devices for injecting air to the retort was carried on. Three such devices were designed and tested. The first, a rather bulky air-gas mixer patterned after that developed in the 6-ton-a-day pilot plant, was not entirely satisfactory, particularly because of metal deterioration and warpage caused by the high temperatures and large temperature gradients encountered in the retort. The original air-gas mixer was replaced by a simple injection device consisting of a perforated pipe covered by an inverted "V". This design was much better than the first with respect to warpage and deterioration of metal, but was troublesome owing to plugging of perforations in the pipe. Subsequently, the pipe was eliminated, and the third injector device consisted of the inverted "V" only. This type proved more practical in operation, although there were indications that oil yield may be slightly lower than when using the perforated pipe and cover design.

Two problems have been encountered with both the second and third type injection devices. Temperature control in the injector itself has been difficult under certain conditions, and deposition of carbonaceous materials has fouled the injectors. The source of the deposits, and possibly an important factor in the temperature control problem, was thought to be the small amount of unseparated oil in the recycle gas. A series of tests, substituting oil-free flue gas from the station's steam plant for that portion of the retort gas normally introduced to the air-gas injectors, improved the temperature control. Several disadvantages were apperent, however, for this procedure complicated the process and degraded the heating value of the product gas.

An exploratory study was made on rates of feeding raw shale, varying from 177 to 328 pounds per hour per square foot of retort bed area (approximately 230 tons per day). There were no apparent process limitations throughout the range of rates tested, and the efficiency of retorting remained high as judged by oil content of the spent shale.

An oil recovery study was conducted to determine the effect of various factors on the efficiency of items of equipment. Other special studies to increase efficiency included one on the patterns of shale and gas flow through a retort vessel under nonretorting conditions.

Refining studies consisted mainly of runs to establish operability or run-length factors for shale oil in thermal cracking equipment. A recycle cracking standardization run was made in the thermal unit on a California petroleum stock to obtain a comparison between the Rifle plant and a commercial installation. Following this an extended visbreaking run on gas-combustion shale oil was made to study visbreaking operability and to prepare a quantity of charge stock for a planned extended run on recycle cracking. Difficulty was encountered with heater-tube coking in this subsequent recycle-cracking run while charging the total naphtha-free visbroken oil, so the stock was distilled to yield a broad gas-oil fraction. This gas oil proved to be a satisfactory charge stock for recycle cracking, and results indicated that good operability could be expected. Thermal refining and chemical treating studies at Rifle were concluded at the end of fiscal 1954. A complete report is being written of all experiments on these units during their 5 years of operation.

In addition to routine control and evaluation work, the laboratory utilized available time and manpower to determine the applicability of established procedures for analyzing shale and its products and to develop new techniques and methods for testing such materials.

An ASTM vacuum distillation method for use on crude shale oil was evaluated, and considerable effort was made to develop a rapid method or methods to detect refluxing conditions in gas-combustion retorts.

A cooperative program with the Atomic Energy Commission to assay oil shale from the Chattanooga area in eastern Tennessee added considerably to the knowledge of the quality of oil shale in that region.

To assist in the guidance of experimental and development programs, economic evaluations are carried out as required on individual segments and completely integrated systems of oil-shale and shale-oil processing. Estimation of the total cost of producing liquid fuels and related products from oil shale on a commercial scale is another function of the evaluation group.

During the past year emphasis has been placed on the study of retorting processes. The economic effect or major operating variables of the gas-combustion process was reexamined. An evaluation was completed on several methods of processing the oil-shale fines rejected from the charge material to the gas-combustion retorting process. A preliminary evaluation was completed on the entrained-solids retorting process being developed by the Oil-Shale Research Branch at Laramie, Wyo. The investment and operating costs for constructing a commercial-scale gas-combustion retort near the present Bureau mine site at Rifle were estimated. A study was made to determine the physical factors which would limit the size of a future oil-shale industry in northwestern Colorado.

A revised estimate is being made of the cost of producing liquid fuels from oil shale, which will incorporate the latest advancements made by the Bureau of Mines in rotary-drilling methods. Previous estimates of mining costs for oil-shale and shale-oil processing systems have included percussion drilling methods.

Laboratories and Pilot Plants, Laramie, Wyo.

Research on retorting small particles of oil shale at high temperatures in an entrained-solids system was advanced in 1954. Although steam normally was used as the entraining medium, a few experiments were made with air which oxidized part of the shale to provide the heat required for the reaction.

A series of experiments was completed in which retorting temperatures were varied between 1,000° and 1,650° F. Although the yield of liquid product decreased with increasing temperature, its quality improved as measured by volatility and aromatic content. More gas is produced at increasing temperatures, a large portion of which consists of C_2 to C_4 olefins. If these constituents can be processed further, several additional gallons of liquid will be obtained from each ton of oil shale.

Destructive hydrogenation is an effective method for decomposing sulfur, nitrogen, and oxygen derivatives of hydrocarbons found in shale oil. Thus, these deleterious elements are removed and the hydrocarbon portion of the molecule retained. During the past year, recycle hydrogenation was studied to prepare maximum quantities of gasoline and catalytic cracking stock from crude oil.

More than 5,700 tests were made to determine the oil yields of cores and drill cuttings provided largely by oil companies and others interested in oil shale resources. A Bureau of Mines Report of Investigations was published on assay logs of 202 sections of oil shale in Colorado, Utah, and Wyoming, assayed or procured from 1945 through 1952.

Research studies continued on the determination of the characteristics and composition of oil shale, particularly its organic component, using extraction, controlled pyrolysis, hydrogenation, and oxygenation procedures.

Composition studies on shale oil originally had been planned to characterize the low-boiling naphtha or gasoline fraction, and to obtain an analysis of the higher-boiling gas-oil which would be the charge stock for cracking processes. Both aims were to be realized with shale oil produced in the N-T-U retort from Colorado oil shale. Retorting research later indicated that high-temperature retorting of shale might also be desirable. A third project then was started for comparing the composition of oils from high-temperature and low-temperature (N-T-U) retorting.

The naphtha study was completed, and a report is being prepared. The gas-oil study has proceeded into the separation stage. Characterization of fractions will be facilitated by newly available analytical techniques, such as mass spectra of high boiling compounds determined by the recently modified mass spectrometer. Data on gas oil have been obtained from infrared and ultraviolet spectra, elemental analysis, and molecular weight determinations. Work on the composition of high-temperature oils was started, and oil from retorting at 1,200° F. has been studied. Work on oils produced at 1,000°, 1,400°, and 1,600° F. will follow.