INTRODUCTION

The Bureau of Mines Synthetic Liquid Fuels Program again forged ahead during 1952, and important technical advances led the way to improved methods of converting coal and oil shale into liquid fuels. Marking the eighth year of activities under this program, the past 12 months brought a new domestic industry nearer realization.

The increasing demand for gasoline and oil and the rising cost of finding new petroleum, coupled with America's growing dependence on imports and the unsettled international situation, have continued to emphasize the importance of the Bureau's Synthetic Liquid Fuels Program. Oil, the indispensable material of wartime, likewise has critical importance in peacetime, touching as it does the life of every individual. Supplementing petroleum with synthetic liquid fuels will not only conserve this Nation's petroleum reserves but also will bring into greater use its tremendous reserves of coal, as well as the vast deposits of oil shale for which no other practical use has yet been found.

The Bureau of Mines Synthetic Liquid Fuels Program is one of the most important and far-reaching of the Government's research projects. Through development of commercial synthetic liquid fuels, the United States can obtain oil products from its great inland reserves of coal and oil shale to supplement petroleum in any quantity that may be necessary, consistent with economic and other requirements, such as national defense. The use of raw materials from such deposits would be of highest importance in wartime, when shipping lanes are menaced by the enemy. The Synthetic Liquid Fuels Program of the Bureau of Mines and research efforts of industry have advanced American technology to the point where it is now possible to begin the design and construction of prototype plants. Certainly, significant improvements will be made as the program continues, but this prospect in no way alters the fact that the start of prototype plants should be encouraged. These plants, as the first step in the development of a synthetic fuels industry, would serve a threefold purpose:

1. Provide a basis for future rapid expansion of the shale-oil and coal processes.

2. Aid in conserving natural petroleum and reducing America's dependence on imports by hastening utilization of abundant domestic raw materials for the production of liquid fuels.

3. Produce commercial quantities of important chemical products at reasonable prices.

Although opinions differ as to when synthetic fuels from coal and oil shale will be needed to supplement domestic oil and imports or when synthetic oil can compete with natural petroleum, national defense needs dictate that we avoid unnecessary risk in a commodity as vital as oil. There is general agreement that this Nation eventually will supplement domestic and imported petroleum with synthetic oil, and the necessary technology must be ready for use without delay.

The United States Department of the Interior has repeatedly indicated its interest in the construction of prototype plants and recommends that, under conditions satisfactory to the Government, aid such as that provided for defense projects under the Defense Production Act be made available to private industry for this purpose. Such assistance is recommended because, although Bureau estimates indicate that both coal-hydrogenation and oil-shale plants could be operated at a profit, the initial plants may not necessarily be profitable enough to attract the required equity capital without Government help.

DEMONSTRATION-PLANT PROGRESS

The synthetic fuels demonstration plants of the Bureau of Mines at Louisiana, Mo., and Rifle, Colo., are of the minimum size that will provide industry with reliable design, operating, and cost data that can be used directly for planning prototype commercial operations. They also produce large enough quantities of finished products of uniform specifications so that practical fleet tests can be made in both military and nonmilitary vehicles.

These demonstration plants are complete operating units, starting with raw materials and ending with finished products; therefore such problems as difficulties in materials handling and waste disposal that might be overlooked in small pilot operations can be solved. During the year work at the Bureau's demonstrations plants was devoted chiefly to solving technical problems and operating difficulties and to improving processes to reduce costs and raise efficiency.

At the Coal-to-Oil Demonstration Plant at Louisiana, Mo., approximately 7,000 tons of coal from two States and 3,000 tons of lignite from another State were converted into synthetic liquid fuels by hydrogenation.1/ Runs on subbituminous coal from Johnson County, Wyo., and Pittsburgh-seam bituminous coal from Washington County, Pa., were followed by a run on lignite from Ward County, N. Dak. Data obtained during the successive runs made possible numerous improvements in the process, mechanical equipment, and plant operation.

Finished commodities also were produced in the Gas-Synthesis Demonstration Plant, which employs a Bureau-developed oil-circulation process.1/ Four exploratory runs were made in this plant, and one important improvement included modification of the unit design for gasification of powdered coal with oxygen. Process design of a 10,000-barrel-a-day gas-synthesis plant was made in an engineering and economic study in cooperation with the National Petroleum Council. Another similar study by the Bureau staff covered the economics of a small coal-hydrogenation plant producing chemicals and fuels.

At the Oil-Shale Demonstration Plant, Rifle, Colo., a new-type oil-shale retort, using the gas-combustion process developed by the Bureau, was constructed on a scale of 6 tons of shale a day.2/ An intermediate pilot unit using the same process now is being constructed and will permit quicker and more detailed experimentation with operating variables on a scale of 50 tons a day. This intermediate unit incorporates some improvements over the 6-ton-a-day unit, such as mechanical shale-handling facilities and complete instrumentation. Further improvements are embodied in the newly completed 200-ton-a-day demonstration plant, which will be put in operation during 1953.

1/ For description of processes, see p. vi.
2/ For description of processes, see p. vii.

A number of different approaches have been used in attacking the difficult problem of refining shale oil, and various solutions offered promise during 1952. Improvements have been made in each of the conventional thermal processes of coking, viscosity breaking, and recycle cracking, and further work is underway on other methods.

In the oil-shale Production mine, the method of mining the 73-foot Mahogany ledge was changed during the year from a three-level to a two-level operation, in which the upper 39 feet will be mined in a single heading operation and the lower 34 feet in one benching operation. In addition to reducing mining costs, the two-level system will provide shale of uniform quality and richness from either bed.

Analyses of oil-well drill cuttings and cores and surface channel samples indicate that Utah oil shale may have possibilities for early commercial exploitation.

PROCESS DEVELOPMENTS

The Bureau laboratories and pilot plants continued their work in cooperation with the demonstration plants to improve existing processes. At the same time, efforts were continued in developing a number of new processes.

In the important field of coal gasification, considerable progress was made in handling slag, an important step toward achieving sustained commercial operations and low-cost gasification.

The pressure-gasification plant at Morgantown, W. Va., was operated successfully at increasingly higher pressures up to 450 pounds per square inch; it provided information for the first time on the beneficial effects of these pressures on gasification of powdered coal with oxygen. The experimental runs showed that increased throughputs are possible under pressure, the capacity at 450 pounds being about 800 pounds of coal per cubic foot of reactor per hour compared with an atmospheric-pressure capacity of only 10 to 20 pounds.

Research on the underground gasification of coal also was advanced considerably during the year as the Bureau investigated new underground systems that permitted steady production of combustible gas for periods up to 3 months. Near the end of the year, an experiment with oxygen demonstrated that synthesis gas of acceptable quality for yielding synthetic fuels, pipeline gas, or ammonia can be produced in an underground system.

At the Bruceton, Pa., laboratories, the first American catalyst for vapor-phase hydrogenation was developed; significant progress also was made on developing a new sturdy, long-lived Fischer-Tropsch catalyst. Developed also at Bruceton was a new process for removing carbon dioxide from synthesis gas, an important purification step in the gas-synthesis process.

High-temperature retorting of oil shale, which offers promise of producing aviation-gasoline components, various important chemicals, or premium-grade gasoline from oil-shale fines, was carried on successfully in a new continuous pilot unit at the Laramie, Wyo., Petroleum and Oil-Shale Experiment Station.

NEW PROCESSES

In addition to the large number of developments on which detailed information will be found in this report, several processes now in an early stage of development may have far-reaching results.

Work has begun on a modification of the coal-hydrogenation process that may permit production of high-test gasoline in a single stage. This process may eliminate some troublesome features of the conventional process in which liquid fuels are produced in a liquid-phase followed by a vapor-phase operation. Virtually complete hydrogenation of bituminous coal has been achieved, with a short reaction time, in batch laboratory tests, and continuous pilot-plant tests are underway.

Preliminary studies indicate that the principle of the fluidized-coal feeder developed by the Bureau of Mines may lead to a practical system of transporting coal long distances in pipelines. Compared with natural gas, about five times as much energy per unit volume in the form of dense-phase fluidized coal could be transported in a coal pipeline as in a natural-gas line under an average pressure of 690 pounds per square inch.

Studies made thus far on retorting oil shale under pressure indicate that this process may have advantages, especially for producing power in conjunction with oil-shale operations.

Experiments late in 1952, with steam and air used alternately for underground gasification of coal, suggest that this classical water-gas-type process may be employed successfully in underground gasification systems developed by electrolinking to produce synthesis gas for ammonia, synthetic fuels, or pipeline gas.

APPLICATIONS OF RESULTS TO OTHER FIELDS

As might be expected, numerous mechanical and process developments of the Synthetic Liquid Fuels Program are being applied to processes other than liquid fuels. One example of this is use of powdered-coal gasification for producing synthetic ammonia. The initial commercial installation was put into operation during the year in Finland, with a powdered-coal gasifier of the same type as that first installed in the demonstration plant at Louisiana, Mo. Industry in this country is also studying the use of powdered-coal gasification for ammonia and other chemicals. Another example is a nitrided Fischer-Tropsch catalyst, which appears to have attractive commercial possibilities for producing chemicals. Synthetic fuels processes yield chemicals as well as fuels, and this phase is being considered by the chemical industry. The first semicommercial-scale coal-hydrogenation plant for the production of chemicals was put into operation by Carbide & Carbon Chemicals Co. during 1952.

COOPERATIVE ACTIVITIES

In keeping with the established policy of the Bureau of Mines, the Synthetic Liquid Fuels Program has been carried on with extensive cooperation of industry, educational institutions, individuals, and other Government agencies. In many cases this cooperation is covered by formal cooperative agreements; others are covered by letters of agreement.

During the year 134 such cooperative projects were in effect, covering coal-to-oil work, oil-shale mining and processing, shale-oil refining, and product testing. Engineering, construction, and equipment companies headed the list of cooperators, with 33 agreements with 28 companies. The work of this group of cooperators included testing by the Bureau of equipment supplied by manufacturers and furnishing oil shale or synthetic fuel products to various companies for processing in their own equipment. The interest of chemical companies in the Bureau's program is evidenced by 21 agreements with 17 different concerns. One of the most important projects in this group was that with Carbide & Carbon Chemicals Co. for processing and testing 75,000 gallons of coal-hydrogenation products from the Bureau's demonstration plant. Oil companies, cooperating both directly and through the National Petroleum Council, have 17 direct cooperative agreements relating to synthetic liquid fuels, with 15 companies participating.

During the year 14 cooperative agreements were in effect with 13 universities. In addition to the agreements, two other institutions, West Virginia University at Morgantown and the University of Wyoming at Laramie, provide facilities on their campuses for Bureau synthetic liquid fuels installations.

Seven coal companies have synthetic fuels agreements with the Bureau, which include the furnishing of coal for conversion to liquid fuels and testing of synthetic Diesel fuel. One railroad, the Denver & Rio Grande Western, is testing shale Diesel fuel in a switching locomotive, and two large natural-gas companies are helping to finance work on the production of pipeline gas from coal.

Notable among the industrial cooperative agreements are those with the Alabama Power Co. for underground gasification of coal at Gorgas, Ala.; with Babcock & Wilcox Co. on the development of powdered-coal gasfication; and with Standard Oil Co. of California, Koppers Co., Inc., and Blaw-Knox Construction Co., which provide resident engineers at the Rifle, Colo., oil-shale project.

An outstanding example of Government-industry cooperation is the work of the National Petroleum Council Committee on Synthetic Fuels Production Costs. Engineers from various oil companies representing the National Petroleum Council Committee and Bureau engineers have carefully studied all phases of design, construction, and operation of oil-shale, coal-hydrogenation, and gas-synthesis plants projected to a commercial scale.

There are many instances of cooperation with other Government agencies. Noteworthy is the fleet testing of coal-hydrogenation gasoline at Camp Lee, Va., which has been arranged by the Office of the Quartermaster General, Department of the Army. More than a quarter-million gallons had been delivered for testing by the end of the year. During 1951 and the first 2 months of 1952, shipments had been made to the Aberdeen, Md., Proving Grounds. Another example is the extension of coal-gasification work to include the production of ammonia synthesis gas from coal. This work was undertaken at the request of the Department of Agriculture, which foresees the necessity of producing synthetic ammonia fertilizer from coal to meet future requirements of agriculture.

Working in cooperation with the Mutual Security Agency, formerly the Economic Cooperation Administration, the Bureau has permitted inspection of its synthetic fuel installations by many foreign visitors and groups. In February and March 1952 the Bureau sponsored a 6-week visit by a group of 16 Europeans, representing France, Germany, Belgium, and England. Included in this group were scientists interested in coal gasification, both aboveground and underground.

The Bureau and the Alabama Power Co., Birmingham, Ala., were joint sponsors of the First International Conference on Underground Gasification of Coal in Birmingham and Gorgas, Ala., February 12-14, 1952. In addition to the foreign visitors, the conference was attended by many industrialists and technicians representing many major companies.

Six principal papers were presented, two dealing with the Bureau's underground-gasification project in cooperation with the Alabama Power Co. at Gorgas, and a review of the work on electrocarbonization of coal, a process originated by the Sinclair Coal Co. and the Missouri School of Mines. Three of four foreign papers reviewed in considerable detail underground-gasification work in Russia, Italy, France, Belgium, and England, and a fourth paper described experimental work aboveground, using oxygen and air in a model system in Belgium.

The Bureau also sponsored a Symposium on Gasification and Liquefaction of Coal in connection with the 1952 Annual Meeting of the American Institute of Mining and Metallurgical Engineers, in New York City, February 18-21, 1952. Experimental work on gasification in the United States and foreign countries was described during two major Symposium sessions, and a panel discussion featured the subject, The Significance of Successful Coal Gasification to the Future of American Industry. Ten papers presented during the Symposium and those of the panel discussion have been published in Gasification and Liquefaction of Coal (published by the American Institute of Mining and Metallurgical Engineers, New York, N. Y., January 1953, 240 pp.).

SYNTHETIC LIQUID FUELS SURVEY

The Nation-wide survey requested by the Department to determine suitable areas for commercial production of synthetic liquid fuels from coal, oil shale, natural gas, and tar sands was completed in 1952 by the Corps of Engineers, Department of the Army, under a contract with the firm of Ford, Bacon & Davis. This survey showed that 25 States have general areas meeting all requirements for one or more commercial synthetic liquid fuels plants. In all, the country has over 200 general areas in which oil can be produced commercially from coal. These areas will support production at any rate up to 15 million barrels of finished products a day. Although only two States - Colorado and Utah - met the requirements for oil-shale operations, these areas could, with favorable mining locations and water currently available, produce shale-oil products at any rate up to 7 million barrels a day. Copies of the individual State reports have been placed in depository libraries receiving Bureau of Mines publications, and a Summary for the United States is available for general distribution.

DESCRIPTION OF PROCESSES

Coal Hydrogenation

In the coal-hydrogenation process for producing liquid fuels and chemicals, hydrogen is forced into the complex coal molecules and oxygen removed so that the chemical constitution is changed to approximately that of petroleum, whereupon the coal substance liquefies. This reaction is accomplished in a liquid-phase operation in which a mixture of pulverized coal, catalyst, and heavy oil from the process is pumped into a high-pressure steel vessel with hydrogen at pressures up to 10,000 p.s.i. After separation of the solid residue of ash-forming material and unliquefiable carbonaceous matter, the lighter products from the reaction are distilled and further hydrogenated in a vapor-phase operation, and the heavy oil is recycled for preparation of the coal-oil paste. The primary products of coal hydrogenation are highly aromatic, and the finished gasoline normally contains 25 to 45 percent of aromatics, including benzene, toluene, and xylenes. Ordinarily, gasoline and liquefied petroleum gases are the only liquid fuels produced, but the product yield can be varied readily - with only slight changes in equipment and operating techniques - to produce jet fuels, Diesel fuel, or heating oils.

Gas Synthesis

The gas-synthesis or modified Fischer-Tropsch process, as developed by the Bureau of Mines, can use as raw material any coal, coke, lignite, natural gas, or other carbonaceous material. The coal or other fuel is first reacted with oxygen and steam to produce synthesis gas, a mixture of carbon monoxide and hydrogen.

After purification, the mixed gases are passed over a solid catalyst at pressures of 20 to 30 atmospheres and temperatures ranging from 300° to 400° F. Under these conditions, the carbon monoxide and hydrogen of the synthesis gas combine to form chiefly liquid hydrocarbons, with smaller percentages of oxygenated compounds and gases. The products vary over a wide range from gasoline, Diesel oils, and heavy fuel oils to solid wax; the yields depend upon the catalyst used and conditions of temperature and pressure.

Oil-Shale Retorting

The Oil-Shale Demonstration Plant, now completed, will employ a Bureau-developed gas-combustion process for retorting oil shale. In this continuous process, crushed oil shale is gravity-fed at the top of the retort and passes down through preheating, retorting, and cooling zones. Recycle gases from the process, which have been stripped of their oil, are introduced at the bottom of the retort and cool the outgoing spent shale. Part way up the retort, after the gases have been preheated, air is introduced through burners to burn part of this preheated gas and further raise its temperature to that necessary for retorting the shale. The hot gases then distill the oil from the shale in the retorting zone, and the oil-laden gases are cooled by the incoming raw shale in the shale-preheating zone. This produces an oil fog, which leaves the retort at about 150° F. and is recovered from the gas stream by simple mechanical separators. The gas-combustion process offers such advantages as continuous operation, no external heating or cooling equipment, little water consumption, and low power requirements.

Following is a summary of 1952 operations at each of the synthetic liquid fuels laboratories and demonstration plants:

Summary of 1952 Operations

Oil from Coal

Demonstration Plants, Louisiana, Mo.

Continuing the testing of American coals and lignite, equipment, and processing techniques, the two Coal-to-Oil Demonstrations Plants near Louisiana, Mo., in 1952 provided added data for the design and operations of prototype commercial synthetic fuels plants. Employing fundamentally different processes - coal hydrogenation and gas synthesis - the two plants convert coal and lignite into high-quality synthetic liquid fuels.

In 1952 the Coal-Hydrogenation Demonstration Plant completed two extended liquid-phase operations and a vapor-phase run. A third liquid-phase run on North Dakota lignite from the Velva mine, Ward County, was begun in November.

In a period of 6 weeks, approximately 4,000 tons of northern Wyoming subbituminous coal from the Lake DeSmet area was converted into 273,000 gallons of vapor-phase charging stock and 65,000 gallons of solids-free heavy oil. The coal was very reactive and hydrogenated readily, but the 30 percent moisture in the raw coal proved to be the controlling factor of the run. As a result, the plant throughput was limited to 60 tons a day of moisture-free coal.

The products of the hydrogenation of the Lake DeSmet coal and of the liquid-phase run on Illinois No. 6 coal made in 1951 were processed in a combined vapor-phase hydrogenation operation. Under terms of a cooperative agreement, 75,000 gallons of the naphtha and gasoline from the Illinois No. 6 stock was withdrawn for tar-acid extraction. The vapor-phase run produced 435,000 gallons of 76- to to 77-octane (Motor Method) gasoline, the bulk of which was shipped for use in military fleet tests, and a smaller amount was used in demonstration-plant vehicles. The run also produced 27,000 gallons of vapor-phase bottoms which was reserved for future wash-oil use.

Pittsburgh-seam coal from Washington County, Pa., was used in the second liquid-phase operation. In about 5 weeks approximately 2,250 tons of coal was converted into 240,000 gallons of vapor-phase charging stock, 116,000 gallons of solids-free heavy oil, and 7,000 gallons of slop oil. The run was considered good, and the coal liquefied readily.

Work was begun late in calendar year 1952 to hydrogenate 3,000 tons of North Dakota lignite containing 39 percent moisture.

Considerable work has been done during these runs to improve the process, mechanical equipment, and performance in the hydrogenation plant. Coal-preparation, accurate coal-weighing, flash-distillation, and reaction conditions in the converters are being improved. Dependable injection pumps were built and proved in service. A tar-acid-recovery unit is being added to the plant.

In the Gas-Synthesis Demonstration Plant, the alumina-lined vertical gasifier was altered to feed the pulverized coal in superheated steam suspension and add the oxygen stream at the burner nozzle. This change proved to be a major improvement and also aided in slag tapping. Three of four exploratory runs extended 9, 7, and 6 days, respectively. Carbon conversion averaged 80 to 90 percent, and the gas contained 40 percent CO and 40 percent hydrogen. To improve refractory life opposite the burner nozzle, two burners will be installed on opposite sides of the gasifier.

Operation of the oxygen plant, Kerpely gas generator, and gas-purification system became routine.

Primary products of the 1952 gas-synthesis run 2 have been processed through the upgrading and distillation facilities. Synthesis run 3 was made in June, with the objective of exploring maximum practical conversion rates without undue deterioration of catalyst. Conversion rates of 85 percent have been achieved.

Engineering and economic studies for commercial-scale operations continued. The process design of the 10,000-barrel-a-day gas-synthesis plant for Western Kentucky coal was completed and accepted by the National Petroleum Council.

A study was prepared comparing the economics of coal versus natural gas for ammonia production. It was concluded that in some parts of the country coal may be economical for production of anhydrous ammonia.

Another study covered the economics of a small hydrogenation plant for the production of chemicals and fuels. It concluded that a plant using 30 tons an hour of Western Kentucky coal could be built with a $38,181,000 capitalization and would show 10-3/4-percent return on 50 percent equity capital after 4 percent interest on borrowed money and after taxes.

<u>Laboratories and Pilot Plants, Bruceton and Pittsburgh, Pa.</u>

Work at the Bruceton, Pa., laboratories and pilot plants on the synthesis of liquid fuels from gasified coal during 1952 included development of an exceptionally sturdy and long-lived Fischer-Tropsch catalyst, of an economical process for the removal of carbon dioxide from synthesis gas, and of a commercially feasible synthesis of alcohols. Particularly important as regards coal hydrogenation were autoclave assays of a number of coals, a new method for predicting the product yield from residual oil, and development of the first American catalyst for vapor-phase hydrogenation.

A new technique devised for activating steel shot and iron turnings has resulted in development of mechanically durable catalysts of long-lived activity, one of which was used for 6 months. The catalysts were oxidized superficially, impregnated with alkali, and reduced before use. Repetition of this procedure after several weeks of use further increased the activity.

Scrubbing hot, impure synthesis gas under pressure with hot, concentrated potassium carbonate proved more economical than conventional procedures for removing carbon dioxide. Data obtained in a pilot plant indicate that less steam is consumed, no heat exchange or cooling equipment is required, the quantity of cooling water is greatly reduced, the scrubbing agent is retained, and loss of desired gases is negligible.

In the oil-slurry process, gradual activation was shown to be necessary for developing maximum activity of the catalysts, whether nitrided or only reduced. Experiments of several months with nitrided-iron catalysts showed that this modified Fischer-Tropsch synthesis yields large quantities of higher alcohols. The process appears to be economically feasible.

Small-scale tests with fused-iron catalysts revealed that complete reduction is unnecessary for maximum activity and optimum selectivity, reduction of less than one-third of the oxide being adequate. Partial reoxidation of a completely reduced catalyst was deleterious to its activity.

Comparison of activities of fused-iron catalysts pretreated in various ways before synthesis showed a carbided preparation to have one and one-half times the activity of a reduced specimen, while a nitrided catalyst was twice as active as the reduced one. The carbide produced the least gas and the largest amount of high-boiling product; the nitride produced the most gas and oxygenated material.

Structural promoters did not affect greatly the selectivity of fused-iron catalysts, and most of them were not advantageous for the activity of nitrided fused catalysts. All but 2 of the 12 tested promoters, however, improved the activity of reduced fused catalysts. In general, the activity of these catalysts increased with the atomic number of the alkali added, a chemical promoter.

The formation of carbides during carburization of iron proceeds in the order hexagonal iron carbide, Hägg iron carbide, and cementite. The first-named carbide is the least stable, and the amounts of each carbide present in a given sample are determined by the temperature and duration of the carburization. Carbide can be preserved during synthesis by using high hourly space velocities of synthesis gas.

The presence of steam in synthesis gas lowers the activity of the catalyst and increases the output of carbon dioxide and methane.

A new method was devised for preparing cobalt hydrocarbonyl, and homologation of tertiary butanol was studied with dicobalt octacarbonyl as the catalyst.

Thermal cracking converted Fischer-Tropsch wax to gasoline, Diesel oil, and fuel oil, and dehydration of oxygen-rich oil over bauxite resulted in raising its octane number by 16 (Motor Method) or 24 (Research Method) points.

In the field of coal hydrogenation, some progress was made in overcoming difficulties in a fluidized-bed reactor. Agglomeration of the powdered coal was eliminated by diluting it with powdered coke.

Autoclave assays were proved to be reliable for predicting the suitability of coals for hydrogenation. One Pennsylvania and seven Colorado coals were thus tested and found to be satisfactory. The yield of distillate, residue, and gas from coking of the residual oil of any hydrogenated coal now can be calculated, obviating the need for coking tests on such oils.

An American catalyst for vapor-phase hydrogenation has been developed. It is at least as durable and active as the original German preparation. Activated carbon, impregnated with molybdenum, was shown to be an excellent catalyst for refining crude shale oil.

The importance of catalysts for coal hydrogenation was demonstrated in autoclave experiments with and without catalysts. For the same extent of liquefaction of coal, the necessary hydrogen pressure in the presence of a good catalyst was a small fraction of that needed when no catalyst was used. Further details of the mechanism of the reaction and of the composition of the products were ascertained.

A method was developed for direct chemical determination of oxygen in organic compounds, and further work was done on separating tar acids from coal-hydrogenation oil by countercurrent separation.

The Bibliography of Pressure Hydrogenation has been printed, and a similar bibliography of the Fischer-Tropsch and related processes is in preparation. Review articles on various current problems have been presented in scientific journals and Government publications.

<u>Coal-Gasification Pilot Plants, Morgantown, W. Va., and Field Tests on Underground Gasification, Gorgas, Ala.</u>

At Morgantown, W. Va., where research is concerned principally with developing economic processes of producing purified synthesis gas for making synthetic liquid fuels, increasing emphasis has been given to pressure gasification of coal as one of the most attractive methods for reducing synthesis-gas costs. The very large quantities of synthesis gas required for synthetic gasoline and other liquid fuels necessitates large-scale gasification of powdered coals with oxygen and superheated steam. The purified synthesis gas accounts for about 70 percent of the cost of the finished gasoline and oil in the gas-synthesis process; and the cost of compressed hydrogen, which can be produced from synthesis gas, represents one-third to one-half the total cost of the product in the coal-hydrogenation process.

Pressure gasification of coal with oxygen offers the advantage of generating synthesis gas at the pressure at which it will be used in a gas-synthesis plant, thereby reducing compression costs. Purification under pressure also has been effected, which makes it unnecessary to reduce the gas to atmospheric pressure for the purification stage.

Results of 32 test runs on the Morgantown pressure gasifier have demonstrated some of the advantages of this process, one advantage being the low cost of raw materials per unit volume of carbon monoxide and hydrogen made. The typical operating results in the body of this report indicate that the large coal throughputs obtained per cubic foot of reactor volume will result in reasonable capital expenditures for equipment. This gasifier has been operated at pressures up to 450 p.s.i.g. and at coal-feed rates of over 1,300 pounds an hour. Alterations of the gasifier and its auxiliaries between runs have improved operability greatly.

The atmospheric-pressure slagging gasifier designed in cooperation with the Babcock & Wilcox Co. has been used at Morgantown for studying a large number of operating variable and design factors. The plant has been operated for 34 runs, testing the effects of various alterations and modifications in design. The data obtained from these tests have been valuable in developing the design of a commercial-scale high-pressure gasifier, particularly in respect to methods for removing slag from the gas stream. The operating data also indicate that, for certain applications, generation of synthesis gas at low pressures will be economical.

Coordinated with the work on the gasification pilot plants, pioneering tests on preheating of the coal-feed stream have been carried out, and strongly coking coals have been preheated to 900° F. without agglomeration.

An oxygen plant capable of producing 7,000 std. cu. ft. per hr. of 99.6-percent oxygen and 25,000 std. cu. ft. per hr. of 99-percent nitrogen has been installed.

Gas-purification work at Morgantown included development of analytical methods for determining mercaptan sulfur, moisture, and dust in synthesis gas. Bench-scale experiments were carried out to study the feasibility of recovering hydrogen sulfide as elemental sulfur from an acid gas stream containing low concentrations of hydrogen sulfide. Experiments also were conducted to study the effect of pressure and carbon dioxide concentration on the adsorptive capacity of activated carbon for carbonyl sulfide (carbon oxysulfide or COS).

As part of a program for investigating the practicability and cost of producing pipeline gas from coal, a bench-scale experiment was made under a cooperative agreement with the Southern Natural Gas Co. on conversion of synthesis gas to methane.

Purification pilot-plant runs were made to study (1) simultaneous removal of hydrogen sulfide and organic sulfur compounds using a copper-chromium-vanadium catalyst, (2) selective removal of hydrogen sulfide from synthesis gas using tripotassium phosphate and Alkacid DIK solutions, and (3) removal of dust from synthesis gas, using a moving-bed coke filter.

Preliminary designs for five buildings that compose the major part of the new Morgantown Experiment Station were transmitted to the architect. Assistance also was rendered with the electrical lay-out for the new station and with the utility piping required by the Synthesis Gas Branch.

At Gorgas, Ala., during 1952 three unit underground-gasification systems using the electrolinking-carbonization process were installed and operated with steady production of combustible gas for periods up to 3 months. The first unit, gasifying coal with air from January until May, produced 95.3 million cubic feet of gas, most of which had a heating value of 83 B.t.u. or more per cubic foot. As the air-input rates were increased up to 1,770 cu. ft. per minute, leakage from the system was high.

The second and third systems were constructed between April and August; and at the end of the year the third system was still producing combustible gas. Gas production from the two units averaged 2.2 million cubic feet of 95-B.t.u. gas per day, chiefly from the second unit in which the maximum air input was 2,040 std. cu. ft. per minute. During most of the operation, leakage from these units varied from zero to 15 percent, compared with a leakage of 48 percent in operating the first unit.

Gasification with oxygen was attempted late in the year in the third system, into which 5.25 million cubic feet of oxygen was pumped to produce a synthesis-type gas having an approximately 1:1 hydrogen-carbon monoxide ratio. Oxygen usage was high, but it is believed that losses can be reduced in further work.

Test results obtained when operating the third unit with alternate air and steam blasts in a manner similar to water-gas-machine operation indicate that it is possible to produce raw synthesis-type gas with a heating value of 300 B.t.u. per cubic foot. During the air blast in the same system, a producer-type gas with a heating value of 104 to 119 B.t.u. per cubic foot was made.

Oil from Oil Shale

Experimental Mine, Rifle, Colo.

In anticipation of increased requirements for shale for operating the gas-combustion demonstration and pilot plants, further improvements were effected in mining techniques in the Production mine (Underground quarry) during 1952, and some equipment was modified to give greater efficiency. Studies were continued on more durable drill bits and efficient drilling methods, and steps were taken to supplement the present air-coursing facilities to meet future ventilation needs.

The Production mine in the 73-foot Mahogany ledge originally was developed on a three-level plan, in which a single heading of 27 feet was mined, followed by two benching operations in levels each 23 feet. As mining technology was developed, it was considered more economical to mine the 73-foot ledge in two levels instead of three, and the change was effected in 1952. In addition to reducing mining costs, mining of the upper 39 feet followed by mining of the lower 34 feet will provide oil shale of nearly the same richness from either level. During 1952 approximately 22,000 tons of shale was removed from the Production mine, and about 2,800 tons of selectively mined shale was delivered to the pilot-plant stockpile for blending in special retorting runs.

Changes in development of the Production mine required alterations in underground equipment. A former scaling rig was remodeled and equipped with an elevating blaster's platform to reach the increased heights of the two-level system, and a multiple-drill carriage was constructed mounting four pneumatic rock drifter drills on a special platform.

In drilling research, the best performance has been obtained with a masonry-type bit, which drilled 766 feet under constant operating conditions at a penetration rate of 83.7 inches per minute at the start of the test and 67.7 inches a minute at the end. Based on a commercial cost of $20 per bit, including five sharpenings, the bit cost for this type is about one-half cent per foot of drilling.

To provide more effective ventilation in the Production mine, construction of a ventilation raise was begun in 1952 in the back of the mine. The raise was completed to a height of 79 feet from the floor; and a connecting incline will be driven to the surface, where an exhausting ventilating fan will be installed when needed. A steel stairway connects the workings with the raise and proposed incline.

Bureau and industry investigations provided further data during 1952 to substantiate the estimates of the partly blocked and inferred oil-shale resources of northwestern Colorado. About 1,000 square miles of the 2,500-square-mile area of the Green River formation is considered to merit commercial development. The area includes a 500-foot-thick measure of oil shale averaging 15 gallons a ton and the Mahogany ledge in the lower part of the measure ranges up to 90 feet in thickness and averages 30 gallons a ton. Estimates indicate a 126-billion barrel reserve of shale oil in the Mahogany ledge alone and 494 billion barrels in the entire 500-foot-thick measure. Investigations on reserves of oil shale in Utah indicate a promising reserve of plus-22-gallon-a-ton shale in the Green River formation, but further data are needed to estimate the reserves of this state and of Wyoming.

Based on theoretical calculations and laboratory studies on the action of roof-stone, it has been concluded safe to mine openings 60 feet wide supported by 60-foot pillars in the Production mine. The original development of the mine called for mine openings 80 feet wide.

Demonstration Plant, Rifle, Colo.

Pilot-plant studies during 1952 were devoted mainly to expanding the scope of experimental data on the gas-combustion process developed by the Bureau at the Oil-Shale Demonstration Plant near Rifle, Colo. A major contribution to these efforts was a 10-day demonstration run on shale of about the grade that would be used in a commercial plant. Satisfactory operation, with a high yield of oil, confirmed previous evaluation tests. Another phase of the pilot retorting work was a process-variable study, a systematic investigation of the effect of shale rate, air rate, and recycle-gas rate on the dependent variables. Data from this study will define the operating characteristics of the process over a fairly wide range. Finally, a process-development program was initiated to examine various ideas for improving the countercurrent, gravity-shale-flow retorting process.

Pilot-plant retorting facilities are being expanded by construction of an intermediate-size gas-combustion unit having a capacity of about 50 tons of shale a day and by erection of pilot refining equipment. The new retort, embodying several improvements over the 6-ton-a-day unit, will be equipped with mechanical shale-handling facilities and complete instrumentation. It will permit a much wider range of operations and will be used to advance process development and to pilot demonstration-scale operations.

Process design has been completed for a small pilot plant designed to furnish fundamental process data on countercurrent, gravity-shale-flow type retorting. More data are required on thermal effects and on the mechanics of overhead removal of product oil from the retort.

Current revisions of the storage and weighing facilities will increase shale storage capacity from 300 to 1,300 tons. The new facilities will meet the requirements of the recently completed continuous demonstration retort and provide accurate weighing facilities, which are essential for obtaining yield data.

A pneumatic conveying system for transferring shale up to 3-inch size from storage to the pilot plant is to be installed and tested under a cooperative agreement with Convair Corp.

Erection of a demonstration-size gas-combustion retorting plant having a capacity somewhere between 150 and 300 tons of shale a day has been completed, but operation of the new unit will not be begun until the early part of 1953, when revision of the shale-handling and weighing facilities will be complete. The rectangular retort vessel is 36 feet high and consists of a steel shell lined with a hung refractory wall. The internal dimensions of the lower half of the vessel are 6 by 10 feet; the upper half tapers and at the top is 5 by 9 feet.

An experimental program has been planned and embodies four major phases: (1) A transition period during which problems encountered in expanding from pilot-to demonstration-plant scale will be solved; (2) the process-development phase for extending studies of particle size of the shale retorted to the range of commercial operations; (3) securing engineering design data for use in designing industry-scale plants; and (4) provision of firm data to serve as the basis of cost estimates.

Demonstration refining operation before 1952 established a general pattern for the operating conditions and equipment requirements for processing shale oil by conventional thermal processes: Coking, viscosity breaking, and recycle cracking. During 1952 intensive studies were made to establish the best operating conditions for each of these operations and to develop combinations of two or more types of operation that might constitute a complete refining procedure. It has been shown that a viscosity-breaking operation may be followed by recycle cracking of the combined liquid product to obtain about the same gasoline yield as that achieved by recycle cracking of the crude. The combined operation permits the major portion of refining operations to be transferred from a point adjacent to the shale deposits to a pipeline terminal near a large center of population.

Work also has been begun on a relatively new refining process, Suspensoid cracking, a compromise between the fluid catalytic technique and thermal methods. Experiments to date indicate that combinations of Suspensoid cracking with thermal cracking may give increased yields of gasoline with little or no reduction in total liquid yield.

Naphtha-treating operations covered a wide range of naphtha types, operating temperatures, and reagent quantities. Experiments were continued on a two-part treatment in which light and heavy naphthas are treated separately and combined after treatment to yield a 400° F. end-point product. In this operation the reagent requirements for the light naphtha are greatly reduced. Studies were continued on the catalytic treatment of shale naphthas, and process design data were prepared for a general purpose catalytic treating unit. All treated naphthas were blended and then leaded in the new tetraethyllead blending unit. The finished gasoline has been used by station vehicles throughout the year, and performance has been excellent.

Cost estimates and process-evaluation studies were made as follows: (1) Systematic evaluation of various processing alternatives possible in the production of fuels from oil shale; (2) economic comparison of three suggested approaches to shale-oil refining, each employing some degree of hydrogenation; (3) a study of the effect of operating the gas-combustion retort under pressure; (4) further investigation of the costs, requirements, and financing of such nonprocess requirements as housing and community development; and (5) study of applications of the gas-combustion-retort process to materials other than oil shale.

The study of the pressurized gas-combustion retort indicates that capital requirements would be greater than for the atmospheric-pressure version of the process, but this may be offset by several desirable effects - greater throughput due to increased density of the retorting medium, suppression of carbonate decomposition, increased yield and higher-value oil, and more economic use of the low-heating-value product gas.

A study of eight treating methods for shale-oil naphtha showed that capital investment would be larger for treating methods using the cobalt-molybdate process than for those using only chemical treating and that the cost of finished gasoline is less by the most favorable chemical treating method than by the most favorable reforming method.

A nomograph was devised to make it possible for any individual to estimate a selling price for shale gasoline at the refinery, using his own judgment with regard to certain items that may vary among different investors or companies. To use the nomograph one must know the scale of production, daily cost of operation, capital requirement, percentages of equity and mortgage capital, percentage of return desired on the equity capital, interest on borrowed money, and income-tax rate.

Greater attention has been focused on using the mathematical approach to planning and programming of research tests and to interpretation of data. Standard statistical methods, such as Latin squares and factorial design, have been found very useful for outlining the most effective research programs, and data interpretation is aided by using multiple correlation techniques.

Laboratories and Pilot Plants, Laramie, Wyo.

Of major importance during 1952 at the Bureau's Petroleum and Oil-Shale Experiment Station at Laramie, Wyo., were completion and preliminary operation of an entrained-solids pilot retorting plant. This system of retorting oil shale, which culminates several years of research and development, promises many important advantages over other retorting methods. The high heat-transfer rates obtained in this system has made possible a shale throughput equivalent to four tons an hour per square foot of retort-tube cross-sectional area. This throughput rate is many times greater than that of moving-bed type retorts.

The principal advantage of the entrained-solids retorting method is the ability to control the quality and type of products. This can be accomplished because of the flexibility of the process to temperature and time variation and control. Very high yields of regular- and premium-grade motor fuels can be produced, as well as critical aromatic chemicals, such as benzene, toluene, and naphthalene and high-octane-value polymers or chemical raw materials from the large volumes of ethylene, propylene, butylene, butadiene, and other gases produced by retorting.

Refining research during the year has included studies of methods for improving the quality of gasolines produced by thermal cracking of crude shale oils or their higher-boiling fractions. A catalytic treating process has been developed to the point where a demonstration-plant unit is being designed for construction at Rifle, Colo. Thermal reforming for improving octane number and acid treating for removing objectionable sulfur, nitrogen, and gum-forming compounds are other naphtha-improving methods being studied.

Solvent extraction and hydrogenation are being investigated as a means of improving feed stocks for further processing and for the production of Diesel fuels. Catalytic cracking of gas oils and high-temperature thermal cracking of crude shale oils or gas oils offer other possibilities for producing high-octane gasoline from shale oil.

Hydrogenation of aromatic gas oils from high-temperature retorting or from high-temperature thermal cracking of N-T-U shale oil has been found to produce high yields of premium-quality gasoline.

Analytical research on the composition and characteristics of oil shale included the improvement of analytical methods, analyses of foreign and domestic oil shales, a study of the constitution of the organic material in Colorado oil shale, and, incidently, examination of the organic material in a trona brine from wells drilled into the Green River oil-shale formation.

Research on the composition of shale oils and their fractions and products from processing has progressed considerably during the past year. At present a pioneering study is being made on the gas-oil fraction from N-T-U crude shale oil. The gas oil has been separated into: (1) A high-nitrogen concentrate, (2) an aromatic concentrate, (3) an olefin concentrate and (4) a saturate concentrate. Identification of the types of compounds in each of these concentrates is underway.

A comprehensive analysis of the naphtha from N-T-U shale oil was completed, and a comparative analysis of naphthas from a number of different retorting processes has been made to indicate the effect of retorting variables on the character of the resulting crude oil.

Considerable progress has been made in developing analytical methods particularly adaptable to shale oil. A method for direct determination of oxygen has been developed, and an organic acid titration procedure for phenols and carboxylic acids is being perfected. Benzoic acid has been identified in the carboxylic acid extract of shale-oil tar acids.