

Bureau of Mines  
Report of Investigations 5043



# SYNTHETIC LIQUID FUELS

ANNUAL REPORT OF THE SECRETARY  
OF THE INTERIOR FOR 1953

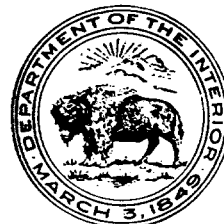
PART I. - OIL FROM COAL

# SYNTHETIC LIQUID FUELS

## ANNUAL REPORT OF THE SECRETARY OF THE INTERIOR FOR 1953

### PART I. - OIL FROM COAL

\* \* \* \* \* **Report of Investigations 5043**



UNITED STATES DEPARTMENT OF THE INTERIOR  
Douglas McKay, Secretary  
BUREAU OF MINES  
J. J. Forbes, Director

---

Work on manuscript completed February 1954. The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is made: "Reprinted from Bureau of Mines Report of Investigations 5043."

# SYNTHETIC LIQUID FUELS

Annual Report of the Secretary of the Interior for 1953

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 1953 has been divided into two separate publications. Each has been published by the Bureau of Mines as a Report of Investigations, and the respective titles follow:

R. I. 5043, Part I - Oil From Coal.

R. I. 5044, Part II - Oil From Oil Shale.

Identical in each report, the introduction summarizes research progress made in 1953 under the entire Synthetic Liquid Fuels program.

A free copy of each 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.

## CONTENTS

	<u>Page</u>
Preface	
Introduction .....	i
PART I - Oil from Coal	
Research and Development, Coal-to-Oil Laboratories and Pilot Plants, Bruceton and Pittsburgh, Pa.....	1
Synthesis of liquid fuels from hydrogen and carbon monoxide ....	1
Process development .....	1
Pilot-plant operations .....	1
Oil-circulation process .....	1
Removal of carbon dioxide from synthesis gas .....	2
Bench-scale experiments .....	3
Catalyst-oil slurry process .....	3
Hot-gas-recycle process .....	4
Catalyst-testing studies .....	4
Fused iron .....	5
Massive iron .....	5
Steel spheres .....	5
Lathe turnings .....	6
Catalyst characterization, kinetics, and reaction mechanism .....	6
Catalyst studies .....	6
Behavior of carbides .....	7
Kinetics of the synthesis .....	7
Reactions of synthesis gas in presence of metal carbonyls .....	8
Analytical methods .....	10
Separation and identification of Fischer-Tropsch products .....	10
Spectrometric analysis of alcohol mixtures.....	11
Sulfur analysis of synthesis gas .....	12
Synthesis of liquid fuels by hydrogenation of coal .....	12
Process development .....	12
High-temperature hydrogenation .....	12
Catalysts for hydrogenation of coal .....	13
Development of vapor-phase catalysts .....	14
Structure of coal .....	15
Carbon-oxygen linkages .....	15
X-ray-diffraction studies .....	15
Analytical methods ...	16
Design and construction of instruments .....	16
Pellet-strength tester .....	17
Slow-rate liquid injector .....	17
Synthesis Gas from Coal Pivor Plants, Morgantown, W. Va.....	19
Experimental development of processes for producing synthesis gas from coal .....	19
Atmospheric-pressure gasifier .....	19
High-pressure gasifier .....	22
Investigations of coal-feeding methods .....	24

CONTENTS (Con.)

	<u>Page</u>
Feeding coal into pressurized vessels .....	25
Injection-burner investigation .....	25
Oxygen plant .....	25
High-ratio centrifugal compressor .....	25
Laboratory-scale experimentation .....	26
Steam-carbon reaction rate .....	26
Gas purification .....	26
Analytical methods .....	26
Bench-scale experiments .....	27
Pilot-plant operation .....	28
Underground gasification project, Gorgas, Ala.....	29
Synthetic Fuels Demonstration Plant, Louisiana, Mo.....	35
Coal-Hydrogenation Demonstration Plant .....	35
Operations - liquid phase .....	35
Liquid-phase run 10 (Pittsburgh-seam coal).....	35
Liquid-phase run 10 (Velva, N. D. lignite).....	37
Description of coal .....	37
Processing .....	37
Performance of equipment .....	40
Removal of solids and heavy-oil recovery .....	40
Multiple centrifugation .....	40
Carbonization .....	41
Precoat filtration .....	44
Operations - vapor phase .....	44
Vapor-phase run 5, Illinois No. 6 coal, Pittsburgh-seam coal, and Velva lignite .....	44
Gas-Synthesis Demonstration Plant .....	47
Coal gasification .....	47
Gas-purification Plant .....	53
Gas-purification data.....	53
1. Girbotol unit .....	53
2. Iron oxide towers .....	55
3. Activated-carbon towers .....	55
4. Kinetics of coal gasification .....	55
Fischer-Tropsch synthesis .....	56
Gas-purification plant .....	57
Synthesis .....	57
Objectives and preliminary preparations ....	57
History .....	58
Catalyst charging .....	58
Induction period .....	58
Normal operation .....	59
Discussion of data .....	59
Activity and disintegration of catalyst ....	59
Product distribution .....	59
Olefin concentration .....	60
Mechanical performance of equipment .....	60
Mechanical seals .....	60
Coolant-oil pumps .....	60
Control valves .....	60
Oil-inlet tee .....	62
Conclusions .....	62
Appendix. Bibliography of papers and reports presented and published in 1953 .....	63

## TABLES

	<u>Page</u>
1. Products from various substrates by reaction with cobalt hydrocarbonyl.....	8
2. Some results of operation of atmospheric gasifier 4.....	20
3. Properties of coals used in tests of atmospheric gasifier 4.	21
4. Typical performance of pressure gasifier operating at pressures of 100, 200, and 300 lb. per sq. in. on pulverized, Sewickley-bed coal.....	23
5. Dust concentration in gas leaving pressure scrubber.....	28
6. Experimental operating results obtained using various types of gasmaking fluids.....	31
7. Operational and yield data; heavy-oil operations, Pittsburgh-seam coal.....	36
8. Analyses of coal and heavy-oil products; heavy-oil operations, Pittsburgh-seam coal.....	36
9. Coal analyses; Velva (North Dakota) lignite.....	37
10. Operational and yield data; liquid-phase processing of Velva lignite.....	38
11. Typical analyses of process streams and products; liquid-phase hydrogenation of Velva lignite.....	38
12. Summary of Bird-DeLaval series centrifugation operations, 24-hr. basis.....	41
13. Analyses of charge materials and product oils; yields obtained in coking Pittsburgh-seam H.O.L.D. and flash pitch.....	42
14. Comparison of methods for removal of solids; liquid-phase hydrogenation of Pittsburgh-seam coal.....	43
15. Data on experimental filtration of Velva lignite H.O.L.D....	44
16. Typical operating conditions; vapor-phase run 5.....	45
17. Typical yields; vapor-phase run 5.....	45
18. Typical analyses of feed and product streams; vapor phase run 5.....	46
19. Summary of gasifier operations.....	49
20. Daily operating summaries; gas-purification plant.....	54
21. Effect of gas conversion feed on product distribution.....	61
22. Products made in synthesis run 4.....	62

## ILLUSTRATIONS

<u>Fig.</u>		<u>Follows page</u>
1.	Aerial view of Bureau of Mines Coal-to-Oil Laboratories and Pilot Plants, Bruceton, Pa.....	Frontispiece
2.	Pilot plant for removing carbon dioxide from synthesis gas.....	2
3.	Cost of gas recirculation.....	4
4.	Magnetic balance for thermomagnetic and kinetic studies of catalysts.....	6
5.	Schematic diagram of batch extractive distillation column with solvent recycle.....	10
6.	Batch extractive distillation column with solvent recycle	10
7.	Bench-scale continuous unit for studying high-temperature coal hydrogenation.....	12
8.	High-temperature coal-hydrogenation pilot plant, showing reactor.....	12

## ILLUSTRATIONS (Con.)

<u>Fig.</u>	<u>Follows page</u>
9. Effect of pressure on specific rate constant .....	14
10. Apparatus for pyrolysis of bituminous coal .....	14
11. Small-angle x-ray diffraction camera .....	16
12. Scales for measuring activity of radioactive samples ...	16
13. Equipment development laboratory .....	16
14. Testing catalyst pellets for crushing strength .....	16
15. Pump for injecting liquids into reactors .....	16
16. Effect of oxygen-carbon ratio on carbon gasification of Sewickley-bed coal .....	18
17. Gasifier 4 design 5 .....	20
18. Pilot-plant flowsheet for gasifier 4 .....	20
19. Pressure gasifier 3 .....	22
20. High-pressure-gasifier method of thermocouple installa- tion at reaction coil .....	22
21. Refractory condition of gasifier 3 following test P-39..	22
22. Pilot-plant flowsheet for gasifier 3 .....	22
23. Coal-feeder flowsheet for gasifier 3 .....	22
24. Simplified flowsheet for slurry system .....	24
25. Simplified flowsheet for steam-pickup system .....	24
26. Typical dust dispersion in synthesis gas .....	26
27. Magnified residue particles in gas leaving atmospheric- pressure gasifier .....	26
28. Effect of pressure and carbon dioxide on adsorptive capacity of activated carbon for varying hydrogen sulfide concentration .....	26
29. Variations in hydrogen and carbon monoxide conversion and calorific value of product gas for methane synthesis tests .....	26
30. Effect of sulfur content of feed gas on catalyst activity .....	26
31. Plan of electrolinking carbonization trials .....	26
32. Vertical gasifier two-burner system .....	46
33. Reactants nozzles, vertical gasifier .....	46
34. Lower section, vertical gasifier two-burner system .....	46
35. Diethanolamine scrubber performance .....	54
36. Diethanolamine scrubbing - typical operation .....	54
37. Simplified flowsheet of synthesis reactor .....	58
38. Daily log, showing variations in synthesis .....	58

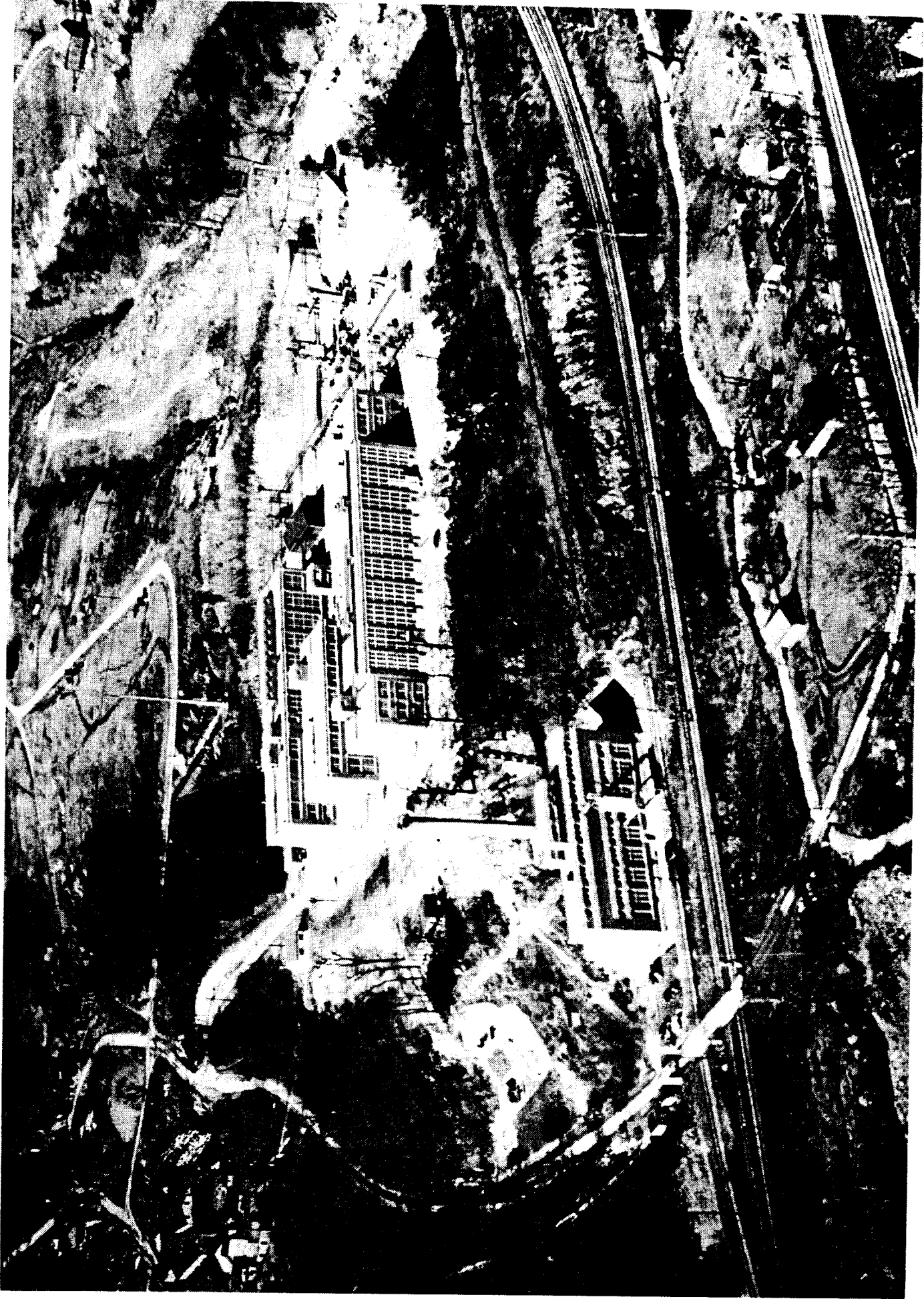


Figure 1. - Aerial view of Bureau of Mines Coal-to-Oil Laboratories and Pilot Plants, Bruceton, Pa.



fuels will be manufactured industrially, there seems to be a large measure of agreement on the need for additional scientific and engineering information basic to future industrial development.)

The most plentiful of our fossil fuels available for production of liquid fuels are oil shale and coal. Although the potential oil production from our important coal reserves is about 10 times as large as that from oil shale, the latter probably will be used in the first synthetic liquid fuels plants because of the appreciably lower cost of production of motor fuel from shale as compared with that from coal. Current cost estimates for motor fuel from oil shale indicate that such fuel may be competitive with that from petroleum in a few years. However, much more research and development will be necessary to insure operable processes and more reliable cost estimates.

The synthetic liquid fuels program has been carefully reviewed by the Bureau and industry technologists; as a result, more emphasis has been placed on fundamental laboratory and pilot-plant research. It was decided that through this type of research the greatest contribution may be made by the Bureau to the future use of coal and oil shale as raw materials for industry. Accordingly, the two coal-to-oil demonstration plants, one using the coal-hydrogenation process and the other gas synthesis, were closed in June 1953. Broadly speaking, the main objectives of these plants were attained by the time the plants were shut down at the end of the fiscal year 1953. Several representative American coals of various ranks had been converted into liquid fuels, using American techniques and equipment. These fuels were tested in automotive engines and military equipment and found satisfactory. The studies indicated that the processes demonstrated were technically feasible but that several years of laboratory and pilot-plant research were needed. It was indicated, however, that the processes "demonstrated" might have immediate economic value if they were used for producing chemicals, in contrast to the production of lower value liquid fuels. In fact, the chemical industry is actually utilizing similar processes for making chemicals from coal.

In addition to discontinuing operation of the coal-to-oil demonstration plants, the Bureau was obliged to recess the research on underground gasification of coal at Gorgas, Ala., at the close of the fiscal year 1953. The data available at that time indicated that underground gasification of coal had definite economic possibilities; however, appropriations were not available in the fiscal year 1954 for undertaking the larger scale work considered necessary for fully evaluating these possibilities.

### Summary of 1953 Operations

#### Oil From Coal

#### Laboratories and Pilot Plants, Bruceton and Pittsburgh, Pa.

At the Bruceton, Pa., laboratories and pilot plants, work on the synthesis of liquid fuels from gasified coal included: Development of exceptionally durable Fischer-Tropsch catalysts prepared by activating massive iron; pilot-plant studies of the hot carbonate process for removing carbon dioxide from synthesis gas and recycled gas; and development of inexpensive catalysts for the slurry-type Fischer-Tropsch synthesis from readily available magnetite ores. In coal hydrogenation, batch-autoclave and bench-scale experiments brought closer to realization a one-step hydrogenation that will directly produce high yields of gasoline. The existing pilot plant has been modified for studies of this high-temperature hydrogenation.

## INTRODUCTION

Under authorization of the Synthetic Liquid Fuels Act of April 1944 (Public Law 290), the Bureau of Mines has operated coal-to-oil facilities at Bruceton, Pa., Morgantown, W. Va., and Louisiana, Mo., and oil-shale installations at Rifle, Colo., and Laramie, Wyo. In cooperation with the Alabama Power Co., it also conducted a series of experiments on the underground gasification of coal at Gorgas, Ala. The program carried out at these stations represents one of the most important and far-reaching of the Government's research projects.

There is general agreement that this Nation will find it necessary in the foreseeable future to supplement domestic and imported petroleum with synthetic oil and that the technology for the production of synthetic fuels from coal and oil shale should be developed at an early date. The advent of any new basic industry, such as synthetic ammonia or synthetic liquid fuels, usually is preceded by a relatively long period of research and development. Indeed, it is difficult to determine when and by whom the fundamental concepts are first disclosed. Usually such concepts are not the result of research directed specifically toward ultimate industrial development, but constitute one of the byproducts of scientific inquiry and experiments which have no applied objective. However, between the time of disclosure of the fundamental concepts and the establishment of an industry stretches a long, tortuous path of planned and uniquely directed effort. The magnitude of such effort is amply illustrated by the history of synthetic ammonia industry of the United States.

Soon after World War I, a large-scale ammonia plant was built; but, because of poor design and operability, the output was insignificant. This unsuccessful plant venture was followed in a short time by establishment of the Fixed Nitrogen Research Laboratory in the United States Department of Agriculture. For more than 2 decades this laboratory provided essential scientific and engineering data as well as new and improved catalysts and designs for high-pressure equipment. The approach to the problem was methodical and persevering, and before the start of World War II the industry was fully developed, with ample capacity. The achievement record of the Fixed Nitrogen Research Laboratory is easily observed in many branches of science and engineering as well as in development of the ammonia industry.

A similar research and development effort on synthetic liquid fuels has been in effect continuously since 1937. Indeed, the similarity to the history of the synthetic ammonia effort is extraordinary. A large "demonstration"-scale coal-hydrogenation plant was built at Louisiana, Mo., and like its ammonia-synthesis analogue at Muscle Shoals, Ala., its operation was discontinued after a few years. Again, the effort has settled down to a program of long-term research and development. Although there are many and diverse opinions as to when and at what price synthetic liquid

In developing massive iron catalysts for the Fischer-Tropsch oil-circulation process, emphasis has shifted from activated steel shot to activated steel-lathe turnings. The loose packing of the turnings and consequently their low resistance to flow have proved advantageous. A hot gas recycle process employing these catalysts appears economically feasible because of the relatively low cost of recycling through a bed of lathe turnings. Methods of pretreating these catalysts were investigated to determine the optimum conditions of activation, such as conditions of oxidation, multiple oxidation, and carburization with synthesis gas or nitriding with ammonia before oxidation.

The process for removing carbon dioxide from synthesis gas under pressure with hot, concentrated, potassium carbonate solution was tested in a pilot plant. Direct comparisons were made of the requirements in both the amine and the hot potassium carbonate processes. The results show that hot carbonate scrubbing requires considerably less steam than the amine process.

In the oil-slurry process a catalyst prepared by impregnating an Allan Wood magnetite ore with alkali has proved as good as the synthetic-ammonia-type catalyst prepared by the fusion method.

The kinetics of the Fischer-Tropsch synthesis on nitrided-iron catalysts is about the same as on reduced-iron catalysts. The rate data can be approximated by a first-order-type of rate equation. Usage of hydrogen relative to total gas (hydrogen plus carbon monoxide) consumed decreased rapidly with conversion, passed through a minimum, and then increased. Consumption of hydrogen and production of methane increased with the hydrogen content of the feed gas. The rate of synthesis increased directly with operating pressure in the range 100 to 300 p.s.i.g.

Studies of the chemistry of metal carbonyls have shown that cobalt hydrocarbonyl has many of the properties postulated for one of the intermediates in the Fischer-Tropsch synthesis. The reaction of acetylenes with dicobalt octacarbonyl often yields crystalline compounds with unique structures resembling, in some respect, the intermediate that has been frequently postulated for the Fischer-Tropsch synthesis.

Quantitative procedures have been developed for separating and characterizing Fischer-Tropsch products, especially the oxygenated molecules. The mass spectrometer has been used in analyzing alcohol mixtures, and detailed analyses can be made for C<sub>1</sub> to C<sub>8</sub> alcohols. In developing a rapid control method for analyzing total sulfur in Fischer-Tropsch gases, sulfur compounds are converted to hydrogen sulfide by passing the gas over a heated platinum spiral, and hydrogen sulfide is determined by the methylene-blue method.

Continuous operation of laboratory-scale equipment for the hydrogenation of coal at high temperatures has been conducted in a small, coiled tube, with molybdenum as catalyst and a coal-hydrogenation middle oil as vehicle. Comparatively large yields of a highly aromatic gasoline were produced in a single step. Modifications of a pilot plant for extension of this work included changes in the reactor and adaptation of the apparatus for use at 10,000 p.s.i.g. pressure.

Batch-autoclave tests of the primary hydrogenation of Rock Springs (Wyo.) coal that has been neutralized with sulfuric acid showed large increases in conversion to benzene-soluble products in the presence of ferrous sulfate, ferrous chloride, and cupric chloride. Sulfuric acid without addition of other catalytic components was a moderately effective catalyst. The initial rate of hydrogenation of Rock Springs

coal impregnated with nickel sulfate was as high as that observed with the most active catalyts. After a short time, however, the rate decreased to a relatively low value.

Studies were continued of the catalytic activity of the individual components of a vapor-phase-hydrogenation catalyst, consisting of acid-treated clay containing small amounts of zinc, chromium, and molybdenum oxides. The clay-like supports used in these catalyts had little refining action, and treatment of the clay with hydrofluoric acid did not appreciably improve either their refining or cracking activity. Zinc or chromium in the presence of clay had little effect, and sulfur appeared to have only a slight hydrogenation action. The principal active component for eliminating oxygen, nitrogen, and sulfur was molybdenum.

The effect of mild air oxidation on the pyrolysis of coal was studied in a laboratory vacuum furnace. Such oxidation greatly increased the amounts of gaseous oxygen-containing compounds evolved during pyrolysis. Both the added oxygen and that originally present in the coal appeared in the gaseous products. Since such results may be expected from peroxidized-ether linkages, this phenomenon suggests the presence of ether linkages in coal.

A literature survey and preliminary experimental work on Debye Scherrer small-angle and x-ray-diffraction patterns of coal indicated that further work will yield valuable information on its structure.

The usefulness of a new method for separating polynuclear hydrocarbons in coal-hydrogenation oils - codistillation adapted to molecular distillation - was demonstrated by separating fluoranthene and chrysene.

Apparatus and laboratory facilities have been obtained for studying isotope-dilution techniques employing radioactive  $C^{14}$ . These will be applied to the analysis of components of synthetic fuels that are very difficult to separate quantitatively by any known procedures.

Several new research instruments have been designed and constructed, including a pellet-strength testing apparatus and a slow-rate liquid-injection pump for small, high-pressure pilot plants.

#### Synthesis-Gas-From-Coal Pilot Plants, Morgantown, W. Va.

The research program at Morgantown, W. Va., is concerned principally with developing processes that will lower the cost of manufacturing synthesis gas and hydrogen directly from coal. The cost of producing synthesis gas, consisting essentially of carbon monoxide and hydrogen, is about 70 percent of the total cost of gasoline by the Fischer-Tropsch process and about 80 percent of the cost of high-B.t.u. gas. The cost of producing hydrogen is about 40 percent of the cost of producing gasoline by coal hydrogenation.

Development work on the atmospheric-pressure gasifier progressed during the year, and industrial application of the process has been shown to be feasible. Many features developed by the Bureau of Mines in the atmospheric-pressure pilot plant at Morgantown are being incorporated by a chemical company in a large-scale gasifier designed to manufacture gas for the synthesis of ammonia.

In 56 test runs made in the atmospheric gasifier during 1953, 1 test using Sewickley bed coal continued for 259 hours. Shorter runs were made with bituminous

coals from Kentucky, Wyoming, and Washington and a Pennsylvania anthracite. The gasifier was modified to prolong refractory life and improve temperature control.

Investigations of the gasification of pulverized coal in the pressure range of 300 to 450 p.s.i.g. continued. For processes requiring compressed synthesis gas, considerable savings can be effected by gasifying coal under pressure rather than generating the gas at atmospheric pressure and then compressing it. Large capacities per unit of volume of reaction space were attained in the pressure gasifier at Morgantown. Various methods of feeding pulverized coal to the gasification equipment are being studied.

Gas-purification work at Morgantown included development of an analytical method for determining carbonyl sulfide in the presence of carbon disulfide, ethyl mercaptan, and thiophene. Experiments were made at atmospheric and elevated pressures to study the removal of hydrogen sulfide from gas by activated carbon and to study the effect of variables on the performance of a moving-bed coke filter for removing dust from gas.

In cooperation with the Southern Natural Gas Co. and the Tennessee Gas Transmission Co., experiments were continued on catalytic conversion of synthesis gas to methane. The specific objective of the tests was to determine the effect of sulfur on a nickel catalyst. In all runs in which sulfur was present in the gas, catalyst activity decreased as soon as approximately 0.58 gram of sulfur per 100 grams of nickel had been adsorbed.

Pilot-plant studies on dust removal showed that water scrubbing in a packed column was an effective means of reducing dust concentration in gas.

#### Underground Gasification Project, Gorgas, Ala.

Gasification operations at Gorgas, Ala., were concluded in December 1952 in the installations in which electro-linking-carbonization had been used to prepare the underground system. The site was flooded with water, and apparently combustion of coal was stopped effectively.

In March and April 1953 plans had been initiated to test a hydraulic method of opening a path through the coal bed; however, before the tests could be made, work at the project was discontinued as the appropriation bill did not provide funds for the fiscal year beginning July 1.

The installations have been maintained in standby condition since June 20. Since that time the Alabama Power Co. has maintained a crew at the project, which has been test-drilled under the supervision of the Bureau. The objective of the drilling is to determine the contours and areas of the underground reaction zones developed during the last experiments. Drilling data indicate that, in sites adjacent to previous underground gasification workings, the electro-linking technique does not always develop straight-line passages connecting the electrodes inserted in inlet and outlet boreholes. Coke residues in adjacent workings apparently modify the electrical characteristics, resulting in radical changes in direction in the preparation of new paths.

#### Oil-From-Coal Demonstration Plants, Louisiana, Mo.

In the coal-hydrogenation demonstration plant, vapor-phase hydrogenation operations were carried out during 1953 on liquid-phase oils from Illinois No. 6 and

Pittsburgh-seam bituminous coals and Velva, N. Dak., lignite. The liquid-phase operation on the Velva lignite had been completed late in 1952, but too late for inclusion in the report for that year.

The vapor-phase hydrogenation operations were started with middle oil from Illinois No. 6 coal and continued with Pittsburgh and Velva charge stocks. The middle oil from the Illinois coal was free of tar bases and tar acids, these having been removed by a private company for a special study under a cooperative agreement with the Bureau. The total time of these runs was 45 days. Except for the Illinois oil, gasoline of essentially the same volume and quality was produced as in previous operations. As the Illinois stock was composed mainly of light-boiling materials low in tar acids and aromatics, a lower octane gasoline was produced.

Over 400,000 gallons of gasoline having an 83-octane number, research method, was produced in the vapor-phase operations. Most of the product was shipped to military installations for testing, increasing to more than 1 million gallons the amount of coal-hydrogenation gasoline supplied by the Bureau for such test purposes.

Temperature control was difficult in the converters during liquid-phase hydrogenation of the Velva lignite. Dry, pulverized coal could not be supplied continuously at the desired rate by the coal-preparation plant, causing erratic temperature control. In this operation, methods of solids removal from the heavy-oil letdown (H.O.L.D.) were investigated and included centrifugation, flash distillation, pre-coat filtration, and carbonization.

The fourth and final operating period of the gas-synthesis demonstration plant was begun November 29, 1952, and continued until January 24, 1953. The vertical gasifier was operated on Illinois No. 6 coal for 9 days in May, and conversion of 87 to 93 percent of the coal charged was attained.

In run 4 of the gas-synthesis demonstration plant, synthesis gas was supplied by the Kerpeley generator operated on coke, steam, and oxygen. Fused catalyst made at the demonstration plant was used, and maximum reactor temperatures were held at 515° F. in the hope that decomposition of the catalyst would not be severe at this lower operating temperature. At space velocities of 480 and 375 per hour, conversions of 84 to 92 percent, respectively, were obtained. Despite the lower operating temperatures, the catalyst decomposed to the extent that the coolant oil contained about 25 percent of ash at the end of the run. About 22,500 gallons of gasoline was made.

Operation of the vertical gasifier in May resulted in much less damage to the refractories in the combustion zone than had been experienced in earlier runs with similar feed rates of coal, steam, and oxygen. Slag was tapped easily every other day. During the run, purification equipment performed well, and the purified synthesis gas contained less than the maximum tolerance of sulfur compounds and dusts.

Operation of the Louisiana demonstration plants was discontinued early in the year, and all units were placed in permanent standby condition. Before the end of the year, the property had been returned to the Department of the Army for disposal of the facilities.

## Oil From Oil Shale

### Oil-Shale Mining Branch, Rifle, Colo.

Production and experimental mining operations were carried on at the oil-shale mine at Rifle, Colo., during 1953. The mining system is being changed to open up the full 73-foot height of the Mahogany ledge in 2 steps. Mining under the new system will yield shale of about the same richness from either the 39-foot top or advance heading or from the lower level 34-foot bench, thus eliminating the need for blending shale at the retort. The mine now is ventilated by an exhaust fan installed at the top of the ventilation raise started in 1952. As an added safety measure, many portions of the mine now have been roof-bolted, and by the end of 1953 more than 4,000 roof bolts had been installed.

To obtain information on oil-shale reserves, 57,900 feet of samples was collected from 16 wells, 1 mine shaft, and 28 core-drill holes in Colorado, Utah, and Wyoming. Revision of previous estimates of Utah oil-shale reserves is indicated in the assay of a core drill from a well in Duchesne County, Utah, which showed a 25-foot-thick section of 26-gallon-per-ton shale. Over 65 percent of the samples collected during the year were from the Green River formation in Utah.

Studies of drilling techniques and blasting methods were continued. The hydraulic rotary test drill was modified to increase the flow of flushing water to the bit, and cooperative work was continued on the design of new masonry-type bits. Increased bit life has been attained at faster drilling rates. Experiments in developing an adequate drill pattern showed that less than one-half pound of explosive could be used per ton of rock blasted.

### Oil-Shale Engineering Branch, Rifle, Colo.

Two gas-combustion pilot-plant retorts with capacities of 6 and 150 tons per day, respectively, are in operation at Rifle, Colo., and construction of a 25-ton-per-day retort neared completion at the end of the year. The capacities are based on a nominal shale rate of 230 pounds an hour per square foot of cross-sectional area.

Further development of the gas-combustion process was the chief objective of pilot-plant retorting activities. Operation of the 6-ton-a-day unit for studying the process variables of shale, air, and recycle-gas rate was continued. Further work is indicated on the application of the principles of mist formation to expand the range of satisfactory operation. In studying an improved method of injecting air to the retort, it was possible to eliminate the mixer section of the conventional gas-air mixer. Temperature was controlled by diluting the air directly with cold product gas before injection to the shale bed. Cooperative retorting tests were made on shale from Chattanooga, Tenn., and from the Paraiba Valley of Brazil. The tests showed the influence of shale characteristics when retorting with the gas-combustion process.

Various pieces of equipment were carefully calibrated and tested before the initial operation of gas-combustion retort 3 (the 150-ton-per-day unit). After some equipment was modified and adjusted, the retort was put on stream, and 5 runs totaling 20 days were made. During this period 2,240 tons of raw shale was processed and 1,075 barrels of oil produced. The unit was operated within a narrow range of air and recycle-gas rates based on data from a process-variable study covering 27 runs in the small gas-combustion retort 1. The results indicate that a reasonable oil

yield and shale rate can be expected after certain processing techniques are improved. The principal difficulties were caused by shale bridging above the air-gas mixers and structural failure of the air-gas mixers due to high temperatures. Better control must be developed to eliminate the bridging problem, and an improved design is being worked out for the air-gas mixer.

Some work on refining methods applicable to shale oil from the gas-combustion retorts was done to complete the current refining studies at Rifle. The crude oil was processed in the thermal and chemical treating units to compare its refining characteristics with those of the N-T-U crude from previous retorts. An extended run on the thermal unit is scheduled to indicate the length of runs that may be expected in commercial plants. Operation of the existing thermal and chemical refining units is to be completed in the fiscal year 1954.

To assist in the planning of the pilot-plant retorting program the economic effects of major operating variables of the gas-combustion retorting process were calculated. A preliminary economic and process-design study was begun on utilization of oil-shale fines rejected from the charge material to the gas-combustion retorting step. The fines (less than 1/4-inch size) represent approximately 5 percent of the total oil shale mined. A major part of this study is evaluation of the entrained-solids retorting process being developed by the Oil-Shale Research Branch at Laramie, Wyo. Approximate costs are being determined for various shale-oil-refining steps. Among the processes being evaluated are thermal cracking, coking, acid treatment of gasoline, and hydrogenation.

In the laboratory unit, detailed analyses were made of oil shales from various sources as a guide for predicting their performance in the gas-combustion retort. The applicability of some pertinent analytical procedures to oil-shale products was examined. Experiments were done on reforming chemically treated shale-oil gasoline by low temperature, vapor phase, catalytic olefin isomerization, and hydrogen transfer reactions.

#### Laboratories and Pilot Plants, Laramie, Wyo.

The heating of particles of shale entrained in a gaseous medium is one of the major studies at the Petroleum and Oil-Shale Experiment Station at Laramie, Wyo. High-quality oils were produced at extremely rapid retorting rates by passing the entrained shale through an externally heated, horizontal tube. The effect of temperature on the yield and quality of products was determined. The oils produced, particularly those obtained at higher retorting temperatures, are much more aromatic than those obtained by usual retorting procedures and are possible sources of premium-quality gasolines and aromatic chemical raw materials.

To provide a basis for a better understanding of the engineering problems involved in applying the entrained-solids technique to the retorting of oil shale, some data on the relationship between the temperature of retorting and the yield and quality of product were obtained. Pilot-plant work based on analysis of several proposed designs of retorts is planned on the engineering problems.

On a laboratory scale, the entrained-solids method has proved satisfactory for retorting Chattanooga oil shales from a deposit in Tennessee and Brazilian oil shale, which, because of its high water content, has been difficult to retort by other methods. The chief purpose of the experiments on the Chattanooga shale was to determine the yield of aromatic hydrocarbons.



Another natural material of local interest as a source of liquid fuels is gilsonite; large deposits occur in Utah. Gilsonite coker distillate was hydrogenated and treated to determine the quantity and quality of gasoline that could be produced. The results indicate that, with the addition of 1.5 percent butane, an overall yield of 95 percent Regular-Grade gasoline can be obtained from this distillate. This is equivalent to about 3 barrels of gasoline per ton of gilsonite.

The assay of oil-shale samples from cores, oil-well drilling operations, and surface sampling has been continued to provide additional information on the oil-shale reserves of Colorado, Utah, and Wyoming. A large number of assays of such samples is being arranged for publication in 1954. Analyses were made of oil-shale samples from Israel to determine their potentialities as a source of fuels in that country, in accordance with the Point Four Program of Technical Assistance of the United States Department of State.

As an aid in selecting more efficient methods for converting oil shale to liquid fuels, research was continued on the characterization of the organic material (kerogen) in oil shale in terms of chemical and physical structure. Oxidation and hydrogenation of kerogen, followed by structural analyses of the products, have yielded some additional information.

Better knowledge of the composition of shale oils is valuable in selecting processing methods. In studies of the composition of shale oil, the nitrogen-containing fraction, which represents about 45 percent of gas-oil portion of shale oil, is being separated into compound types and analyzed by various chemical, adsorption, and spectrometric methods.

Studies of the composition of N-T-U shale-oil naphtha are being completed. Separation and identification of the phenols, carboxylic acids, and nonthiophenic types of sulfur compounds in the naphtha are now under way. Results of this work and of previous work on the hydrocarbon, nitrogen, and thiophene sulfur constituents will complete the characterization of this naphtha.

New analytical methods, such as type analyses of oxygenated compounds and the application of new spectrometric techniques are being developed.

## PART I - OIL FROM COAL

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

Work at the Bruceton, Pa., laboratories and pilot plants (see fig. 1) on the synthesis of liquid fuels from gasified coal included: The development of exceptionally durable Fischer-Tropsch catalysts prepared by activating massive iron; pilot-plant studies of the removal of carbon dioxide from synthesis gas and recycled gases by the hot-carbonate process; and the development of inexpensive catalysts for the slurry-type Fischer-Tropsch synthesis from readily available magnetite ores. In the field of coal hydrogenation, batch-autoclave and bench-scale experiments indicate the possibility of developing a one-step hydrogenation that will directly produce high yields of gasoline.

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

##### Process Development

##### Pilot-Plant Operations

##### Oil-Circulation Process

The oil-circulation process, developed by the Bureau of Mines, has very effectively overcome one of the major difficulties of the Fischer-Tropsch process, the removal of the large exothermic heat of reaction, 7,200 B.t.u. per pound of product. This process, in which the catalyst is completely immersed in oil, is one method for adequate dissipation of the heat of reaction which is removed from the catalyst as sensible heat of the liquid. Some of the energy can be recovered in an external heat exchanger by generation of high-temperature steam. Because of the cementation encountered with fused catalysts in fixed beds, the linear velocity of the circulating oil was increased until the granules of catalyst were subject to gentle agitation. A life of 4 to 5 months resulted for catalysts of adequate mechanical stability.

Fused, promoted magnetite, although active catalytically, disintegrated after about 1,000 hours of use. Such deterioration led to a variety of operating difficulties, and a more durable catalyst was sought. Activated commercial steel shot, 1/32 to 1/16 inch in size, was found to be an effective Fischer-Tropsch catalyst. Runs as long as 6 months were made; but at the end of that time, most of the active catalytic surface had been lost. This spalling of the coating apparently was aggravated by the slow but constant physical abrasion and attrition of the moving shot in the agitated bed. Because of the large void space in a bed of lathe turnings (85 percent compared with 50 percent for the granular magnetite and steel shot), use of a fixed bed became possible without danger of cementation. As a result, the flow of cooling oil could be reduced, as agitation of the bed was no longer required, less mechanical attrition occurred, and the pressure drop through the bed was lower.

Lathe turnings were activated before synthesis by oxidation with steam at 600° C. (to convert 20 percent of the iron to magnetite), impregnation with a solution of potassium carbonate, and reduction in hydrogen at 450° C. A porous, catalytically active surface was thereby formed, supported on an inert core of massive iron. With lathe turnings, the amount of iron in the active zone was greater than with steel shot, because of the higher degree of oxidation (20 percent as compared

with 5 percent) and the greater external surface area of the turnings. Thus, only one-third as much iron was required for the same extent of conversion of synthesis gas.

A striking contrast between lathe turnings and fused iron oxide is the greater chemical stability (resistance to oxidation) of the turnings. These were used for long periods at 270° C., a temperature at which the fused catalyst would rapidly disintegrate. However, between 270° and 290° C., some oxidation of the lathe turning took place. Operation at these temperatures was possible when the catalyst was reactivated periodically by oxidation and reduction.

Carburization of the turnings is being investigated as a means for obtaining a still more active catalyst that will operate below 270° C. at high gas flows. When reduced iron was carburized with synthesis gas, carbidic and elemental carbon were deposited in the active layer. Upon subsequent reoxidation, most of the carbon was removed as carbon dioxide. Such a catalyst, after reduction, was more active than those activated only by oxidation and reduction. Other methods of activation under study are: Varying degrees of initial oxidation, multiple oxidations, nitriding, and use of alloy steels. Ultimate goals are to make maximum yields of gasoline and to achieve high overall conversion of synthesis gas by either single-pass or multi-stage operation.

Because high yields of gasoline and low yields of gas ( $C_1$  plus  $C_2$ ) are essential in commercial production of liquid fuels, the effects on product distribution of the wax content, of the circulating oil, of temperature, and of the alkali content of the catalyst were studied. The wax content in the cooling oil was allowed to increase from the usual 32 percent to 78 percent by controlling the amount of reflux from the overhead condenser. Production of gasoline rose from 51 to 65 percent of the  $C_3+$  hydrocarbons, and the yield of wax dropped from 18 percent to 9. These changes may have been due to cracking of wax, although the temperature was lower than that used commercially in petroleum cracking. A more plausible explanation is that the high quantity of wax retarded formation of additional wax. When the wax content of the cooling oil was reduced to the usual low value, the gasoline and wax yields returned to their original values. Despite the greater yield of gasoline, the yield of gas remained constant.

The yield of gasoline was also increased by operating at a higher temperature, 290° C. However, higher yields of gas were obtained and the durability of the catalyst would probably be unsatisfactory under these conditions.

Variation of the potassium content of the turnings, by injection of alkali into the converter, also shifted distribution of the product. When the potassium content was increased from 0.013 to 0.037 percent, the amount of gas dropped from 45 grams to 30 (per cubic meter of gas converted), and the yield of wax rose from 3 grams to 27. There was no major change in the total gasoline plus diesel-oil fractions. Although injection of alkali had been tried by German investigators, its effect had been very temporary. In this case, the effect was permanent.

#### Removal of Carbon Dioxide From Synthesis Gas

Removal of carbon dioxide from synthesis gas in both the gasification and synthesis steps is necessary to achieve high conversion of carbon monoxide and hydrogen to liquid products. The best existing method for removing carbon dioxide is to use solutions of ethanolamines to absorb this gas. Because steam alone, needed for regenerating amine solutions, adds about 2 to 3 cents to the cost of a gallon of liquid fuels, an improved process is being developed in which a hot, concentrated