

## INTRODUCTION

For 11 years, under authorization of the Synthetic Liquid Fuels Act of April 5, 1944 (30 U.S.C. 321-325), and amendments, the Bureau of Mines has carried on an extensive research and development program to establish methods for producing oil from coal and from oil shale.

This act was passed by the 78th Congress primarily because of the stress of wartime demands for liquid fuels to supply our armed forces during World War II. The act was progressively extended by the 80th and 81st Congresses, as later peacetime demand for oil and oil products continued to increase.

When this program was begun, domestic production of petroleum was ahead of demand, and net exports were about 7 percent of the production. In the years since, although domestic demand has increased about 70 percent, production has not increased at the same rate. Imports of oil have increased since 1948, until net imports are about 10 percent of domestic production. Looking ahead, it is believed that the gap between demand and domestic production of petroleum will widen. Therefore, increased reliance must be placed on importation over long sea lanes, or liquid fuels must be supplied from such substances as coal and oil shale.

New reserves of petroleum in the ground are being discovered only with increasing effort and expense. The present price differential in favor of natural products as compared with synthetic products is expected to become less as a result of the relatively diminishing natural supply and of continuing research that will increase efficiency in production and lower the final cost of synthetic fuels.

The Congress authorized a total of \$87,600,000 for this research program on synthetic liquid fuels between 1944 and 1955. During the 11-year period the Bureau of Mines obtained basic-research, engineering, and cost data in preparing for the time when such information will be needed by a synthetic-liquid-fuels industry. To carry on the research and development, the Bureau built and operated 3 laboratories and 2 engineering plants. Of the 3 Bureau laboratories, that at Laramie, Wyo., deals with oil-shale problems; the one at Bruceton, Pa., is studying coal-to-oil processing; and the third laboratory, at Morgantown, W. Va., is concerned with the conversion of coal to gas. In addition, gasification of coal underground is being studied in a cooperative project at Gorgas, Ala., on the property of the Alabama Power Co.

Work has also been conducted to demonstrate shale- and coal-to-oil processes on a larger scale. An experiment station at Rifle, Colo., was constructed to develop methods for mining, retorting, and refining oil from oil shale. At Louisiana, Mo., the conversion of coal to oil by direct hydrogenation and by the Fischer-Tropsch process was demonstrated. The larger plants have served the purpose of showing that American oil shales and coals can be processed to liquid fuels and that American equipment can be adapted to and devised for these purposes. At the same time, personnel has been trained in operating such plants, and valuable cost data have

been obtained. Industry is now operating or planning plants of similar size for coal hydrogenation and shale-to-oil processing. The first pioneering stage is thus passed, even though prevailing prices do not encourage large-scale production of synthetic fuels in the United States at present.

Looking ahead, however, it is becoming more widely recognized that domestic supplies of natural petroleum cannot satisfy the ever-increasing domestic demands. Within the near future American oil supplies may begin to be supplemented by synthetic fuels from oil shale or from coal. The research being continued now as part of the regular program of the Bureau of Mines aims to improve the processes and to develop new ones; all will aid in conservation and wise utilization of our mineral resources. This continuing research will advance the time when it will be economical for synthetic liquid fuels to supplement the natural liquid fuels used in our factories, tractors, automobiles, and aircraft.

For current work in this field the Bureau of Mines needs no special authorization and no extension of the Synthetic Liquid Fuels Act was requested. As the act expired in April 1955, this volume is the last annual report of the Synthetic Liquid Fuels series. It covers results obtained through May 1955. Work done in the entire 11-year period will be summarized in a comprehensive report to be issued soon.

Progress on further research and development, which will be carried on by the Bureau's coal and oil laboratories, will be reported hereafter in the annual reports on work in these fields. As in the past, specialized papers concerning research on particular topics will be presented as Bureau publications in technical journals.

#### SUMMARY OF OPERATIONS DURING JANUARY - MAY 1955

##### Oil From Coal

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

Research was continued to provide both fundamental and engineering data on the production of synthetic fuels from coal by the Fischer-Tropsch process and by coal hydrogenation. With each process, work has ranged from the large-scale pilot plant through medium-scale bench tests to small-scale laboratory study.

In Fischer-Tropsch pilot-plant production of high-octane gasoline over nitrided-iron catalysts, engineering evaluation indicated an economic advantage from blending alcohols (produced in the synthesis) with the gasoline fraction. The data for this work were derived, in part, from a test on a nitrided, fused-iron catalyst in the oil-circulation pilot plant; the catalyst was active for more than 3,700 hours and produced large yields of high-quality gasoline that had an octane number of 92.9, or 98.5 after addition of 1 mililiter of tetraethyl lead per gallon. The nitrided catalyst was considerably more stable than the same catalyst in the reduced state.

In bench-scale experiments with the catalyst-oil-slurry Fischer-Tropsch process one of the major problems has been agglomeration of catalyst particles on the reactor walls. Addition of high-molecular-weight alcohols to the suspension oil has decreased the tendency toward agglomeration, as was found to be true also of forced circulation of the slurry by either gas lift or a turbine pump.

Small-scale experiments were conducted to develop methods for preparing and pretreating massive iron catalysts made from steel turnings and steel wool.

Carburization of these catalysts with carbon monoxide increased the activity sizably, but reduced massive iron catalysts had greater activity than the corresponding nitrides or carbonitrides. Fused-iron catalysts containing a variety of structural promoters were prepared from Alan Wood magnetite; but none of these preparations, in either the reduced or the nitrided states, had greater activity than the original magnetite.

Factors influencing the activity of fused-iron catalysts in both the reduced and nitrided forms were studied. The activity increased with decreasing particle size to a limiting value for particles of 28- to 32-mesh or smaller. The surface area decreased sharply with increasing reduction temperatures; but the activity appeared to be independent of reduction temperature, except that the activity of nitrided catalysts decreased at the higher reduction temperatures. For a given reduction temperature the activity of reduced catalyst increased with the extent of reduction up to a limiting value at about 40-percent reduction. With nitrided catalysts the activity increased continuously with the extent of reduction.

A laboratory study has been begun on sulfur poisoning of iron catalyst. The approach will be twofold: Prepoisoning of the catalyst by known concentrations of sulfur compounds dissolved in liquid hydrocarbons and poisoning by exposing the catalyst to known concentrations of sulfur compounds in the synthesis gas.

Continued fundamental study of the chemistry of the oxo process has included the use of infrared spectroscopy to elucidate the structures of cobalt carbonyls and hydrocarbonyls. In another study the complex molecules formed by reactions of acetylene with cobalt or iron carbonyls are being investigated, because similar products are believed to occur as intermediates in the Fischer-Tropsch process; information about them may help to explain the mechanism of this synthesis.

The synthesis gas used as raw material for the Fischer-Tropsch and other processes must not contain excessive amounts of carbon dioxide or of hydrogen sulfide. Pilot-plant studies of the hot carbonate process for purifying synthesis gas have been extended to include simultaneous removal of carbon dioxide and hydrogen sulfide. About the same maximum efficiency of removal (97 percent) was obtained for these two impurities; however, hydrogen sulfide was removed more completely when the concentration of carbon dioxide was low.

The second major phase of work at Bruceton is investigation of the coal-hydrogenation process for direct conversion of coal into gasoline. In pilot-plant studies of high-temperature coal hydrogenation much trouble has been encountered in controlling the temperature and in avoiding formation of "coke". Many of these difficulties have been solved by installing a paste preheater and by developing improved instrumentation and operational techniques, including internal cooling by hydrogen. In the modified pilot plant, temperature control during hydrogenation was possible in the range 400° to 520° C. However, "coke" formation occurred at the higher temperatures, even though no excessive temperatures were observed.

Bench-scale studies of hydrogenation of middle oil in the presence of powdered ammonium molybdate were made in a small, coil-type reactor. The results suggest that virtually all of the gasoline obtained from a coal-oil paste, under similar conditions, originates from middle oil rather than from coal.

The effect of mineral matter on the hydrogenation of Rock Springs, Wyo., coal and the influence of sodium hydroxide on coal hydrogenation were studied in batch autoclaves. Neither the mineral matter originally present in a commercial Wyoming

coal nor the special acid washing required to remove most of it had more than a slight effect on the hydrogenating characteristics of the coal. With the same coal, hydrogenation in the presence of sodium hydroxide produced about the same yields of light and heavy oil as in the absence of the alkali, but the yield of asphaltene decreased, and some hydrogen appears to have been produced in the overall reaction.

Hydrocarbonization of coal aims at hydrogenation of dry coal to produce either oil or high-B.t.u. gas and a dry char that may be used to produce synthesis gas, hydrogen, or power. In earlier work coal particles had agglomerated in the reactor; in new bench-scale studies, Rock Springs coal again agglomerated when heated rapidly in hydrogen to temperatures above 400° C. However, a free-flowing char could be produced at 700° C. by first subjecting the coal to stepwise hydrogenation at 400°, 500°, and 600° C.

Continuing fundamental studies on the structure and chemistry of coal are supported by Bureau of Mines and cooperative funds. One recent approach in such studies is via the action of microorganisms on coals; yeasts, molds, and bacteria have been isolated from North Dakota lignites; and certain cultures from oil-soaked soils are apparently able to utilize chrysene and light-oil bottoms from coal-hydrogenation oil. The formation of coallike materials by heating or by acid treatment of organic compounds has resulted in useful generalizations regarding the structures required for forming a coallike char. A powerful reducing system for organic molecules, lithium in ethylenediamine, has been investigated. This system should be particularly useful for low-temperature hydrogenolysis of coal because ethylenediamine is one of the best solvents for low-rank coals. X-ray diffraction studies of benzene-insoluble residues from coal hydrogenation indicate that these residues are coallike but more ordered than the original coal.

#### Coal-to-Gas Laboratories and Pilot Plants, Morgantown, W. Va.

During January to May 1955 no pilot-plant work on coal gasification was possible because the high-pressure plant was being completely rebuilt at a newly constructed station. New equipment was installed for the study of various methods of feeding coal to gasification reactors operating at high pressure.

Extensive data on gasification in both atmospheric-pressure and high-pressure pilot plants had been accumulated before the new station was opened. These results have been evaluated, and reports are being prepared. In general, the data show that, at the same oxygen/carbon ratio, gasification was highest and materials requirements lowest for the lowest rank coal.

Raw gas as produced from coal must be purified before use. In gas purification, work was done on dust determination and removal. Methods are being developed for determining the ultimate particle-size distribution of a dust and for determining size distribution as it actually exists in a gas stream. The latter value is a better criterion for the performance of dust-removing equipment. Both methods are satisfactory, except for very fine particles.

Dust-removing equipment is being evaluated. A high-pressure scrubbing tower has been fabricated so that dust removal can be studied under controlled conditions, and a counterflow feeder is being developed for use with dry-dust-removing equipment.

In connection with desulfurization of gas, molecular sieves (aluminosilicates) were evaluated to determine their effectiveness in removing carbonyl sulfide and

hydrogen sulfide from gas streams. Under the test conditions these adsorbents were not as effective as activated carbon.

In cooperation with the Atomic Energy Commission, various possible types of reactors have been considered for gasifying coal by nuclear energy. A bench-scale, electrically heated reactor packed with refractory-coated spheres to simulate a conceptual design for a nuclear reactor was designed for exploratory engineering study.

A study of the steam-carbon reaction showed a relationship of rate of reaction of steam and powdered graphite with decreasing particle size at 2,400° F. A new high-temperature reactor is being constructed to extend the work to 3,500° F.

Studies are being made on the effect of variables on the micronization of coal during the flashing of coal-water slurries in externally heated tube coils. Gasification of coal-water slurries is under investigation in a coiled-tube furnace that is electrically heated by passing a current through the coil. At 1,850° F. high yields of gas were obtained with only 1/10-second contact; a subbituminous-coal slurry yielded gas that contained 65 percent of the total carbon.

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

Field-scale experimentation on the underground gasification of coal has been conducted to determine whether it is feasible to bring the chemical constituents or the energy of coal to the surface in gaseous form, which may be used for the synthesis of liquid fuels or other purposes. Since June 1954 the Bureau of Mines, the Alabama Power Co., the Stanolind Oil & Gas Co., and the Halliburton Oil Well Cementing Co. have cooperated in testing hydraulic fracturing of coal in place and then using the fractures to pass air through the coal bed and gasifying the coal in place.

Hydraulic fracturing was applied to the America coal bed at Gorgas. An extensive area was fractured and the permeability increased approximately 100-fold, which was enough to permit a gasification trial. Air-injection holes were bored down to the fractured coal bed, and the bed was ignited. Combustible gas was produced at the injection well soon after ignition and has now been produced almost continuously for 4 months. Various operational difficulties have been encountered in obtaining adequate capacity and control.

#### Oil From Oil Shale

##### Oil-Shale Experiment Station, Rifle, Colo.

At the Oil-Shale Experiment Station, Rifle, Colo., work under the Synthetic Liquid Fuels program of the Bureau of Mines continued for the first part of 1955. Outstanding achievements during this period were development of a rotary-drill heading jumbo for use in mining oil shale and solution of several engineering problems encountered in further development of the gas-combustion process for continuous retorting of Colorado oil shale.

All mining activity was stopped on February 28, 1955, owing to a roof failure and fall. No underground work has been accomplished since that date. However, two geophones and a recorder were installed in the area where the roof failure took place. The recorder is in continual operation, and a running daily chart of the microseismic noise level has been kept.

Before the mine was closed the mining and transportation of shale were in progress at an accelerated rate. Development of the bench level was also being carried on. No production has been made by benching, but all preparations for the breakthrough were completed.

Collection of samples from core holes, gas wells, etc., continues. The samples are transported to the Petroleum and Oil-Shale Experiment Station, Laramie, Wyo., for assay. Oil-shale reserves are calculated and included in the overall reserve picture. The subcontour structure and isopach maps are extended and corrected to include new information.

Shakedown tests were completed on a new rotary-drill heading jumbo, and testing of the drill and various types of bits was underway at the time the mine was closed. The incomplete tests showed that the overall performance of the drill was good. More comprehensive tests are necessary before a complete evaluation of the drill unit will be possible.

To blast down oil shale on a large scale it is necessary to drill holes and place the proper amounts of explosives. In the work at the Rifle oil-shale mine every drill round is experimental, and the hole patterns and blasting mediums are varied. A program to study long-hole heading blasts was in progress. One 30-foot slab round and one long-hole cut round were drilled and blasted. The longer, 20-inch sticks of blasting dynamite are easier to handle and speed the loading of drill holes. The hydraulic-powered boom and work platform have reduced the number of man-hours required to charge a large round with explosives. Indications point to early development of long-hole heading blasts.

Studies of new mining methods included a plan and design in some detail of one referred to as a sublevel bench-stopping method. This plan consists of driving adits at both the top and bottom of a panel in the minable bed of shale, with draw points above the lower adits. A narrow shelf is excavated from the upper adit, and mining carried on by vertical drilling of the shelf and blasting down of the oil shale, which is loaded into trucks at the draw points above the lower adits. A cost estimate for this plan indicates a higher cost per ton of shale and a lower extraction ratio for the proposed new system.

Three gas-combustion pilot plants with capacities of 6, 25, and 150 tons per day, respectively, based on a nominal shale rate of 230 pounds an hour per square foot of cross-sectional area, have been in operation at Rifle, Colo. Each plant had its particular functions. The 6-ton-a-day pilot plant was used largely for fundamental process studies, such as investigation of combustion-zone reactions. The newer 25-ton-a-day plant had been geared closely to the 150-ton-a-day plant to pilot new ideas developed from the small pilot plant and to work out more expeditiously and cheaply the problems arising from operating the large plant. The 150-ton-a-day plant was designed to produce process and engineering data on a large enough scale to provide confident extrapolation to semicommercial or commercial application.

In general, the overall retorting program for the first half of 1955 was determined by: (1) The problems that developed from operating the 150-ton-a-day plant, (2) the completion of shakedown tests of the newly constructed 25-ton-a-day retort and then integrating its operation with the other units conducting retorting studies, and (3) the continued search for understanding of the fundamental mechanisms of the process on the 6-ton-a-day retort.

The operation as reported last year on the 150-ton-a-day plant was exploratory in nature, designed to learn something of the general operating characteristics of the plant. Since then, operability and quality of the data improved to a point that it was decided to make a special 5-day evaluation run. In general, the run was quite successful. Operation of the plant was smooth, and the data were excellent. However, oil recovery amounted to only 84 percent of Fischer assay, which was low compared to the potential yield indicated by pilot-plant work. Analysis of the data indicated that the loss could be attributed to a less efficient oil-recovery system and to an abnormal amount of secondary cracking for the larger unit. In an effort to solve this problem, a retorting program using a narrow particle range of 1 to 2 inches was begun, and the previous wide range of 3/8- to 3-inch shale temporarily abandoned. Operation of the large plant at conditions similar to those of the 5-day standard run showed a negligible increase in product oil recovery and about the same amount of secondary cracking continued to exist. Further tests are being made in an effort to determine better operating conditions.

Although the narrow particle-size range tests were being conducted on the large plant, an exploratory program was carried out on the 6-ton-a-day pilot plant to evaluate the effect of three narrow particle-size ranges at similar operating conditions to the large plant; these were 1/4 to 1/2 inch, 1/2 to 1 inch, and 1 to 2 inch.

The outstanding observation from these tests was that, on 1- to 2-inch shale, oil recovery was lower than was expected, and oil properties showed signs of secondary cracking similar to that of the large plant. This was contrary to previous operation on the small plant. The only significant difference found was a high dilution-gas rate. As a result of these tests, a more extensive program was initiated on the small plant to determine operating conditions necessary to give satisfactory oil recovery with 1- to 2-inch shale. These data are now being analyzed. However, the effect of a high versus a low dilution-gas rate was readily apparent. A high dilution-gas rate produces a lower maximum bed temperature and an undesirable high combustion zone. The low dilution-gas rate produced a higher maximum bed temperature and a lower combustion zone. Oil properties improved correspondingly at the lower dilution-gas rate.

Because of distributor temperature limitations of the 150-ton-a-day plant, a low dilution-gas rate could not be maintained; however, low dilution-gas rates had been successful in the 25-ton-a-day retort. Accordingly, a program was initiated on this unit to develop a satisfactory distributor. Two distributors have been developed. The first consists of 2 perforated pipes, 1 over the other, to improve temperature control, and the second distributor is identical to the first, except for a refractory cover to protect the distributor metal further.

Further oil-mist nucleation studies were also made in an attempt to improve oil recovery. A program was initiated to develop an outside nuclei generator that could be operated independent of the retort. Two methods were tried. The first involved vaporizing solid sodium chloride by hot flue gas and then injecting the vapor stream into the retort via the recycle-gasline where rapid quenching resulted in the production of fine salt-crystal nuclei. Although the system did work, difficulty was experienced in operating the equipment. The second method was an aluminum chloride generator. Anhydrous aluminum chloride was vaporized and then injected into the recycle-gasline. The aluminum chloride reacted with water vapor in the recycle gas to form nuclei of aluminum hydroxide. This method also was effective. However, because the cost of aluminum chloride is high, development of a suitable sodium chloride generator seems more practical at this time.

A series of tests was conducted on the 6-ton-a-day pilot plant to determine whether the beneficial effect of minimizing secondary cracking when adding sodium chloride solution to the shale was caused by actual nucleation or by the sodium chloride acting as a combustion catalyst. Several additives were tried with a range of catalytic activities and vapor pressures. It was concluded from the study that the addition of sodium chloride does function by nucleation rather than by combustion catalysis.

A comprehensive statistical study of the effect of all process variables on the combustion zone characteristics and the effects if any on the retort performance was made. The 6-ton-a-day plant was used for this work. The following conclusions were drawn: (1) Shale rate or recycle-gas rate had little effect, (2) dilution-gas rate was very critical in positioning and setting the intensity of the combustion zone, (3) air rate also affected the position of the combustion zone and its intensity, (4) dilution gas composed from gas from the retort was more effective than steam (at the rates studied) to achieve good retort operation, (5) larger shale particles tended to give a less desirable combustion zone at some combinations of process variables, and (6) higher bed height tended to improve combustion-zone characteristics.

#### Petroleum and Oil-Shale Experiment Station, Laramie, Wyo.

The application of modern techniques for fluidized flow of solid particles to the process of retorting oil shale has possibilities that need to be fully explored. Oil-shale retorting research at the Laramie Station for the past several years has included studies of retorting oil shale, utilizing entrainment of small particle size shale in steam, air, or gas and, to a lesser extent, using fluidized beds.

During the period of this report additional data have been obtained on auto-thermic retorting, in which the shale was entrained in air rather than steam. By this procedure all or part of the process heat can be obtained by combustion of a portion of the organic matter in the shale or its decomposition products.

Additional experimental work was begun to compare the yield and quality of products obtained by entrained-solids retorting of oil shale at various temperatures with those obtained by thermal cracking of shale oil, produced by conventional retorting, under similar operating conditions in the same apparatus.

Refining research was centered around the hydrogenation either of crude shale oil or distillates produced by coking crude shale oil, and the cracking and reforming of products from hydrogenation. Thermally cracked naphthas were hydrogenated at various temperatures, using different catalysts to determine the most suitable conditions for reducing their nitrogen and sulfur contents and increasing their octane numbers. The best overall results were obtained with cobalt nolybdate catalyst at 400 p.s.i. over the temperature range of 900° to 1,000° F.

Crude shale oils were hydrogenated at 3,000-p.s.i. pressure over cobalt molybdate catalyst at various temperatures. The quantity and quality of the products varied with the temperature, a gasoline meeting regular-grade specifications after adding TEL being produced at 1,010° F. The more paraffinic naphthas produced at lower temperatures need to be reformed to meet commercial gasoline specifications. Preliminary studies of methods for reforming these naphthas are underway. An experimental program to determine the yields and quality of products produced by a combination of hydrogenating, cracking, and reforming of shale-oil coker distillate was completed.



During this reporting period 3,446 oil-yield determinations were made on samples derived principally from cores and drill cuttings from the Green River formation of Colorado, Utah, and Wyoming. A report on the oil yields of sections of Green River oil shale in Colorado being compiled jointly by the Laramie and Rifle Stations is expected to be completed by July 1956. The report will include oil-yield logs of sections drilled in 1953-55 and tabulations of the actual oil yields of samples representing the 15-gal.-per-ton sections of all oil-shale cores drilled up through 1954 in Colorado.

Studies were continued of the amount and ultimate composition of the organic material in Colorado oil shale. Additional studies of the separation of shale components by the use of sonic energy, mechanical shaking, ultracentrifugation, and mulling were not particularly successful.

Research continued on studies of the composition of the organic component of oil shale. Solvent extraction and hydrogenation and oxidation degradation procedures each contributed additional information helpful to solution of the problem. A report, Constitution of Organic Acids Prepared From Colorado Oil Shale, Based Upon Their n-Butyl Esters, has been completed for publication.

Shale-oil-composition studies during this period have been directed toward two major objectives: Characterization of the gas-oil fraction from N-T-U shale oil and comparison of oil produced at different retorting temperatures. The N-T-U oil is representative of shale oils produced at low temperatures, so the composition of its gas-oil fraction (which is feed stock for cracking processes) should aid in solving problems associated with the production of fuels from such shale oils. If shale oils are to be produced at higher retorting temperatures a knowledge of the changes in composition resulting from the retorting temperature should prove helpful in designing refining procedures. An integral part of both investigations has been development of adequate separation and analytical techniques, particularly for the higher boiling-range fractions.

The technique developed to separate the N-T-U gas oil in fractions containing few enough components for analysis was described in a published report, Application of Separation Techniques to a High-Boiling Shale-Oil Distillate. The principal methods used were molecular distillation, thermal diffusion, and adsorption.

Selected properties of fractions from the high-temperature retorted oils (particularly those produced at 1,000°, 1,200°, and 1,400° F.) are being determined and used to establish the composition of each fraction. The composition of each crude oil may then be calculated from the composition of its fractions. A number of the lower boiling components have been identified in terms of individual compounds and the quantity present in the crude oil. The crude oils also were analyzed by the Bureau of Mines routine method to obtain a general knowledge of the character of the oils. These analyses showed that the aromaticity of the oils increased with increase in retorting temperature, as did the content of the parent compounds of various homologous aromatic series.

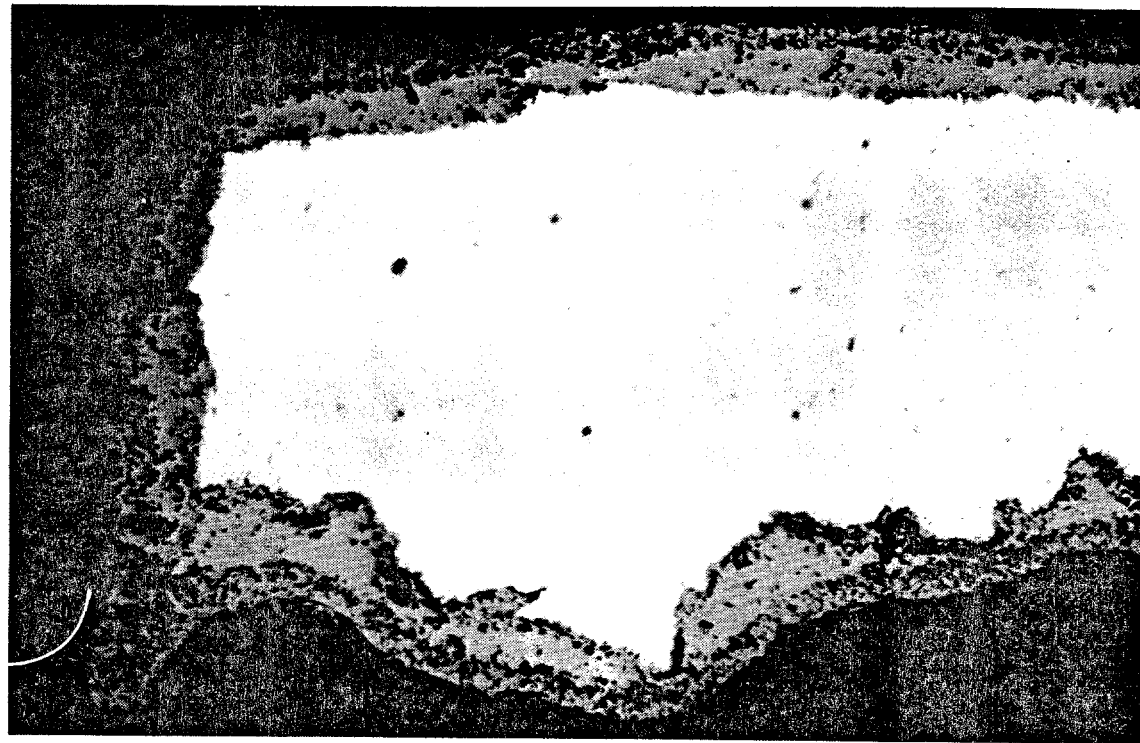
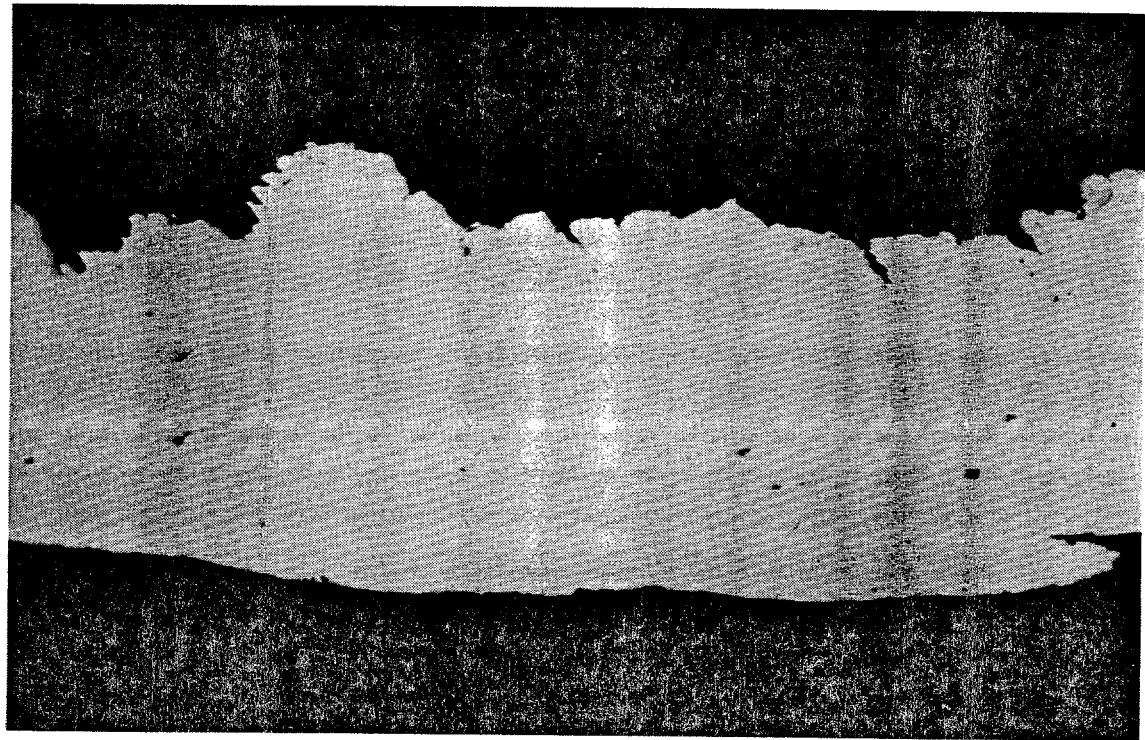


Figure 1. - Photomicrographs of cross section of iron turnings for use as Fischer-Tropsch catalyst:  
original turning (left) and turning activated by oxidation (right), x 125.