

## CHAPTER 2. - SUMMARY OF RESEARCH ON SYNTHETIC LIQUID FUELS FROM COAL

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As authorized by the Synthetic Liquid Fuels Act of April 5, 1944, and amendments, the Bureau of Mines was responsible for an extensive experimental program, including work in demonstration plants, on producing liquid fuels from coal, oil shale, and agricultural residues. The act expired in April 1955; research on synthetic liquid fuels since that date continues as part of the regular Bureau investigations on coal and on oil shale. This report, however, presents accomplishments of the work with coal only for the period of the special Synthetic Liquid Fuels Act.

The major subjects of coal research studied under the program - gasification, gas purification, coal hydrogenation, and Fischer-Tropsch synthesis - are stages of processes in which coal is virtually completely converted to fluid fuels, such as gasoline and oils. Carbonization of coal was not included in this program because its major product is coke, and the liquids produced are essentially byproducts.

## Gasification of Coal

Bureau of Mines Contributions, 1944-55

With the cost of clean, compressed gas amounting to 50 to 80 percent of the cost of synthetic gasoline from coal, Bureau of Mines work was aimed at developing a process for obtaining lower cost synthesis gas (a mixture of carbon monoxide and hydrogen suitable for making synthetic liquid fuels) by gasifying pulverized coal. Basic studies were made on the thermodynamics of coal gasification and on the kinetics of the steam-carbon reaction, considering the effects of residence time, concentration of oxygen, particle sizes, and geometric surface areas.

Bench-scale studies with a slurry of powdered coal and water in an externally heated coil-reactor showed that approximately 65 percent of the carbon in a subbituminous C coal could be gasified in a residence time of only one second at 1,850° F.

Pilot Studies of Gasification Processes. - On a larger scale in a pilot-plant gasifier the steam was preheated to about 3,500° F. in pebble stoves to supply heat for the steam-carbon reaction. Approximately 2 pounds of preheated steam was fed to the reactor per pound of carbon. Although technically feasible, the method proved uneconomic because of mechanical difficulties in obtaining highly superheated steam; furthermore, contamination from coal ash made the life of pebbles short.

Concurrent experiments in a small-scale gasifier showed that continuous gasification of powdered coal in entrainment with oxygen and steam would be feasible. Coals of all ranks could be gasified, but younger coals of high oxygen content allowed considerably higher carbon conversion and substantial reduction in oxygen requirement.

In the first design, with reactants introduced tangentially, the refractory lining was eroded severely. A second atmospheric-pressure gasifier was built with a burner that mixed coal, steam, and oxygen at the point of entry; minimized danger of flashbacks; and improved the life of the refractory lining by reducing to a practical minimum impingement of reactants on the lining. Three types of coal were tested at various ratios of oxygen:carbon and steam:carbon, and at different coal rates. A subbituminous C coal required the lowest amounts of oxygen and steam and anthracite the highest, with a bituminous coal intermediate. Heat loss from the gasifier was highest for anthracite and lowest for subbituminous C coal, in line with the lower reaction temperature for the more reactive coal. The same relative order of heat loss would occur also in a large-scale commercial gasifier, but surface losses would become smaller in proportion to the total energy involved.

A high-pressure pilot-plant gasifier was designed to produce synthesis gas more cheaply by gasifying 500 to 600 pounds of coal per hour at 20 to 30 atmospheres pressure. Reactants were introduced through the top of the gasifier, and firing was straight downward; nevertheless, the refractory lining slowly eroded. The gasifier was then redesigned with a completely water-cooled

reaction space. Slag accumulating on the cooled surface was expected to prevent erosion and provide thermal insulation. However, with bituminous coal the slag layer was too thin, while with high-ash anthracite culm, slag built up in the chamber. The cooling unit will need to be designed for the specific coal being gasified.

A pneumatic coal feeder was developed and used for both atmospheric-pressure and high-pressure gasification. Pulverized coal, fluidized by flowing gas, was charged to the gasifier at uniform rate.

An important aspect of the continuing work is a cooperative study with the Atomic Energy Commission of the use of nuclear heat (as a substitute for partial combustion of coal) to provide the energy for gasification. The first step will be a study of materials needed for the special high-temperature equipment.

### Gasifiers in the Demonstration Plant

Pulverized coal was gasified on a larger scale in the Bureau's demonstration plant. During experimentation a dependable standby source of synthesis gas was provided by a commercial Kerpely gas producer, modified to use oxygen instead of air in the otherwise conventional gasification of coke. This unit produced 80,000 to 95,000 standard cubic feet (std. c. f.)<sup>5/</sup> per hour of synthesis gas as required for the Fischer-Tropsch-synthesis plant.

The first experimental gasifier was a horizontal Koppers Company unit designed to handle 1 ton of pulverized coal per hour in nonslagging operation at atmospheric pressure. Variables studied included the ratio of oxygen to coal, coal particle size, the length of burner nozzles, the method of adding steam, and the ratio of steam to coal. A significant variable was found to be the ratio of oxygen to coal; conversion of carbon increased nearly linearly with increase in the oxygen:coal ratio. In one 265-hour period of operation some 250 tons of coal was used in producing 15,700,000 cubic feet of CO + H<sub>2</sub>.

A second experimental gasifier was an upright cylinder, lined at first with rammed aluminum oxide and planned to handle 3,000 pounds of coal per hour. Pulverized coal was picked up by the oxygen stream and carried in a fluidized state into the gasifier, through a nozzle located tangentially slightly above the bottom of the cylinder. Superheated steam was injected separately nearby.

In early runs high rates of conversion to gas were obtained, but there was difficulty from flashbacks in the oxygen-coal stream and from erosion and peeling of the refractory lining. Refractory material accumulated in the slag and led to further difficulty in removing the slag.

The unit was revised to use superheated steam to pick up the coal; the steam-conveyed coal was then fed through the center pipe of a nozzle around

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<sup>5/</sup> Throughout this chapter, in discussions of gasification and gas purification, volumes of gas were calculated, according to a gas-industry standard, as dry gas at 60° F. and 30 in. Hg.

which oxygen entered through an outer annular pipe. The damaged lower portion of the refractory lining had to be replaced periodically, even after reducing impingement by changing the burner angle and eventually installing a second nozzle so that the two flames would merge. However, operation with steam-conveyed coal was satisfactory mechanically, and slag was tapped intermittently without difficulty, allowing substantially continuous operation. In a final run carbon conversion was 87.6 to 93.3 percent. Raw coal fed at 1,900 to 2,000 pounds per hour produced 62,000 to 68,000 cubic feet of synthesis gas.

### Underground Gasification

Underground gasification tests, first attempted by the Bureau of Mines as means of obtaining synthesis gas, are being continued for other possible uses of the gas, such as burning in powerplants. Field-scale tests have been conducted in cooperation with the Alabama Power Co. in a high-volatile A bituminous coal at Gorgas, Ala. The first test utilized previously mined paths. Gas obtained from the exit holes had heating values varying with the kind of blast provided but below values desired, probably because of insufficient contact of the reactants along the path underground; some of the carbon monoxide (produced from the coal) burned in the unreacted oxygen.

Later experiments explored possible means for maintaining better contact between reactants. In some tests with mined passages between entry and exit holes the product gases had heating values at times up to 100 B.t.u. per cubic foot. Longer paths increased coal consumption and decreased the quantity of excess oxygen, but the underground passage apparently was still too large for enough contact between reactants. There was also excessive leakage from the underground system.

Smaller underground paths were prepared in electrolinking-carbonization experiments, in which connections were established between electrodes spaced at various distances (up to about 150 feet) in boreholes drilled to the coal bed. A current passed between such a pair of electrodes developed an electrical path, and the coal was carbonized to a porous coke through which air or oxygen could be blown. Gasification with an air blast after electrolinking-carbonization produced totals of up to 99.6 million cubic feet of producer-type gas, with heating values of 71 to 86 B.t.u. per cubic foot.

Blasts of oxygen, or alternately air and steam, produced richer gas. Over a quarter of the heat of combustion was probably still being lost underground.

Another approach toward preparing restricted flow paths for gasification was hydraulic fracturing of a coal bed, the fractures radiating from a central borehole. Gasification was then initiated; air was admitted at nearby borings, and gasification products were withdrawn from the injection hole.

### Gas Purification

Raw synthesis gas made from coal contains both dust and gaseous impurities. Before the gas can be used to manufacture synthetic liquid fuels it must be

freed of most impurities, particularly those that might poison catalysts in the Fischer-Tropsch synthesis. The Bureau's gas-purification research aimed at developing purification processes, operable at pressures up to 450 p.s.i., for removing dust and reducing the total sulfur content of raw synthesis gas below 0.1 grain per 100 std. c. f. and the carbon dioxide content below 4 percent by volume.

Laboratory studies were made on the impurities found in gas from various coals, and analytical test procedures were developed or adapted for determining the presence of these impurities.

In studies on processes for removing dust particles from the gas, tests were made of a ring-packed scrubber, an electrostatic precipitator, and a moving-bed coke filter. The filter usually removed 86 to 95 percent of the dust remaining after electrostatic precipitation, leaving such low concentrations as 0.004 to 0.1 grain per 100 cu. ft. Dust-removing devices were tested in connection with both the atmospheric-pressure and the high-pressure pilot-plant gasifiers.

Experiments on the removal of organic sulfur compounds from gas showed that adsorption on activated carbon at elevated pressures could substitute for the alkalized-iron process that had been used in Germany. Activated carbon reduced organic sulfur to less than the specified limit of 0.1 grain per 100 cu. ft. and could simultaneously remove carbonyl sulfide and small quantities of hydrogen sulfide. Other experimentation was concerned with simultaneous removal of hydrogen sulfide and carbon dioxide by scrubbing the gas in aqueous solutions of diethanolamine.

Another approach toward removing sulfides and carbon dioxide from synthesis and other gas was provided by a process newly developed in a Bureau of Mines laboratory, employing a 30- to 45-percent solution of hot potassium carbonate at elevated temperature and pressure. Absorption and regeneration (by depressuring and steam stripping) occur at about the same temperature, so no heating and cooling are required between steps. This elimination of heat exchangers helps to reduce the cost of scrubbing pressurized gas to less than that of similar purification by amine solutions. In some pilot-plant tests the process lowered the carbon dioxide content of synthesis gas from 10 percent to 0.6 and hydrogen sulfide content from about 0.5 percent to 0.025 and completely removed small concentrations of carbonyl sulfide.

Satisfactory purification of synthesis gas on a large scale was accomplished in the Bureau's demonstration plant. A three-step purification process was used to treat 2,000,000 cu. ft. per day of gas containing 16-20 percent of carbon dioxide and 100 grains of sulfur per 100 cu. ft. The purified gas contained only 2-5 percent carbon dioxide and less than 0.01 grain of total sulfur per 100 cu. ft. This plant-scale treatment involved, first, bulk removal of hydrogen sulfide and carbon dioxide in diethanolamine, then removal of residual hydrogen sulfide by passing the gas downward through beds of iron oxide on wood chips, and finally removal of organic sulfur compounds by passing the gas downward through beds of activated carbon.

## Coal Hydrogenation

As developed largely in Germany by Bergius and later by I. G. Farben-industrie, coal hydrogenation involved a liquid-phase stage, in which powdered coal was made into a paste with heavy oil; catalyst was added; and this mixture (with added hydrogen) was injected into reactors at 250 to 700 atmospheres (3,700 to 10,300 p.s.i.) and up to 480° C. (896° F.). The heavy product was the oil used in making the coal paste. The lighter product ("middle oil") was used in the vapor-phase stage; the oil and hydrogen were injected at 300 atmospheres, through a preheater-vaporizer, into fixed-catalyst-bed reactors. The oil was saturated and refined in a first step and then converted to gasoline in another step. Catalysts were later developed for converting middle oil to gasoline in one step at 700 atmospheres.

### Basic Research

Bureau of Mines work on coal hydrogenation included fundamental studies on the structure, chemistry, and microbiology of coal; laboratory and pilot-plant development of processes; and operation of a large-scale demonstration plant. Basic studies included examination of infrared spectra of many coals and chars. Anthraxylons from bituminous coal of the same rank from various parts of the world produced the same infrared spectra, while those of different rank produced somewhat different spectra. Chars from various natural products, organic compounds, and polymers were studied to find the mode of formation and structure of chars that resemble coal and to obtain ash-free coal-like model substances for investigation. X-ray diffraction patterns of several 400° C. carbohydrate chars resembled those of bituminous coal.

### Characterization of Coal-Hydrogenation Products

Separation and identification of products have been essential for evaluating synthetic fuel processes. Special methods were developed for handling various kinds of products, such as polynuclear hydrocarbons. Infrared and mass spectrometric methods were adapted to qualitative and quantitative analysis of liquid and gaseous products from hydrogenation. Chemical and physical studies were made of the phenols in the liquid product from hydrogenating coal.

### Autoclave and Related Experiments

In autoclave studies many American coals were found suitable for hydrogenation to liquid fuels. A North Dakota lignite, coals from Colorado, Wyoming, Illinois, Kentucky, and Pennsylvania, and gilsonite yielded 70 to 80 percent of benzene-soluble oils in iron-catalyzed hydrogenation. Catalysts were much more active when impregnated on coal from aqueous solution than when added to powdered coal as powders. Other experiments suggested that some inorganic constituents, found in whole coal but not in anthraxylon, acted as moderately active hydrogenation catalysts. Hydrogenolysis of anthraxylon indicated that asphaltene is an intermediate product in coal hydrogenation.

Conversion of coal to liquid and gaseous products at 400° C. (752° F.) appeared to be a first-order reaction with respect to the benzene-insoluble matter