

CHAPTER 6. - HYDROGENATION OF COAL

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Brief History and Status of Coal Hydrogenation Before 1944

Coal was liquefied in the laboratory by the action of hydriodic acid in 1869 (8), but it was not until 1914 that addition of hydrogen to coal was considered as a process for industrial conversion of coal into a liquid fuel. At this time, commercial development of the Bergius concept (2, 3, 7, 52) of direct addition of hydrogen under pressure and pyrolytic temperature conditions was undertaken (6). World War I and many technical difficulties hampered progress, but in 1919 a small 30-ton-per-day continuous unit was put in operation splitting high-sulfur crude-oil residues, and subsequently, in 1922, liquefying coal. During the following 3 years some 200 coals were tested, mostly in autoclaves and in a 1-ton-a-day continuous auxiliary unit. Oil yields were low (4) and need for further development was recognized (5), but the feasibility of large-scale production of oil from coal had been demonstrated.

Independent research by I. G. Farbenindustrie led to separation of the hydrogenation process into two steps - the liquid- and vapor-phase stages (26) - and to the discovery of sulfur-resistant catalysts for use in the vapor phase. In 1927 the first commercial-scale plant was put in operation by this company, which subsequently took over all research and development work in Germany on coal hydrogenation.

Progress was slow because of adverse economic conditions and the many technical difficulties, but by 1939 hydrogenation capacity had reached 1,400,000 metric tons of liquid product yearly. Germany's war economy aided development of the industry, and by 1944 (when the Synthetic Liquid Fuels Act was passed in this country) 18 hydrogenation plants were processing coal and coal tar in Germany, and production had reached a peak of 4,000,000 metric tons of liquid product yearly (42). This hydrogenation product supplied the bulk of German aviation fuel; however, bombing rapidly reduced output after May 1944.

England too had become interested and in 1935 had put into operation the first commercial plant to process bituminous coal; but the vulnerability of plants to air attack (36) was probably instrumental in curtailing expansion of the industry in that country. Developments in Japan are somewhat obscure; it is probable that only small semiscale plants (21) and one hydrogenation plant of commercial size ever got into operation there (53).

The processes employed in these industrial installations have been described in the literature (26, 35, 42, 53). Basically, the original Bergius principle of coal liquefaction and the I. G. Farben. concept of two-phase operation were retained, but tremendous improvements were made in catalysts, equipment, and process techniques. Briefly, the processes were as follows:

In the liquid-phase stage, dry, powdered coal was made into a fluid paste with about an equal weight of heavy oil (made for this purpose in the process), and meanwhile catalyst was added. Paste and a large excess of hydrogen were compressed to 250 to 700 atmospheres pressure (3,700 to 10,300 p.s.i.) and preheated to reaction temperature by heat exchange with hot process streams and by convection heating in a gas-fired furnace. The stream then was injected into a series of three to five reactors in which the reaction temperature (480° C.

or 895° F., maximum) was controlled by introduction of cold hydrogen as needed. For the production of gasoline, the time and temperature of reaction were controlled to yield the maximum of middle oil or vapor-phase feed consistent with production of enough heavy oil for making coal paste; for fuel-oil production, ~~an excess of heavy oil was produced. The effluent from the reactors then~~ passed into a hot separator where it was separated into a gaseous stream containing the lighter hydrogenation products and a heavy oil (H.O.L.D.) containing the unliquefied coal, catalyst, and coal mineral matter. The H.O.L.D. was continuously withdrawn, processed to remove the solid materials by centrifugation and carbonization of the centrifuge residue, and used in paste making.

The gaseous overhead stream from the hot separator was cooled by heat exchange with process streams, and the condensed liquid product was removed from a cold separator for later fractionation into (1) a middle oil of 332° C. (630° F.) end point for vapor-phase processing; and (2) a residue boiling above 332° C., which was blended with H.O.L.D. for centrifugation and paste making. Phenols produced in the hydrogenation were extracted from an appropriate naphtha cut, which was then reblended with the middle oil. The gaseous hydrogen stream from the cold separator was washed with an appropriate oil cut from the hydrogenation product to prevent accumulation of the gaseous diluents in the stream, and was recycled to the hydrogenation system.

Vapor-phase conversion of middle oil to gasoline was much simpler than the liquid-phase stage. Essentially, the middle oil and lighter oils from the liquid-phase operation were blended and, along with an excess of hydrogen, injected at 300 atmospheres (after preheating to reaction and vaporizing temperature) into series of two to four fixed-catalyst-bed reactors. Reaction temperature was controlled by admission of cold hydrogen at various levels of the catalyst beds. A two-step process was used in most plants. A saturation step with pelleted tungsten sulfide catalyst, at about 404° C. (760° F.), removed nitrogen and oxygen and furnished refined stock for the second or splitting step, with tungsten sulfide-on-Terrana (a fuller's earth) catalyst at 449° C. (840° F.), in which actual conversion to gasoline occurred. As in the liquid phase, the high-pressure hydrogen stream was recycled, but wash-oil scrubbing was not needed in the vapor phase. A water wash after the saturation step, to remove ammonia, was all the purification required. One-step conversion was practiced to a limited extent only with oils of low nitrogen and oxygen content, as these elements, in the form of ammonia and water, were harmful to the catalyst.

Ammonium molybdate, and tin chloride (or oxalate) plus a volatile halide, were first used as catalysts in the liquid-phase stage at 250 to 300 atmospheres pressure. Later these scarce materials were replaced by crude iron oxides and ferrous sulfate, which were found suitable for brown coals at 300 atmospheres (4,400 p.s.i.) and for bituminous coals at 700 atmospheres (10,300 p.s.i.) operating pressure. Operation at the higher pressure permitted increased throughput and improved coal utilization, warranting change to this pressure even for processing brown coals; a short time before the outbreak of the war new liquid-phase plants were planned and built in Germany for 700-atmosphere operation.

Vapor-phase operation at 700 atmospheres facilitated use, in a small plant, of a common hydrogen recycle with the liquid phase eliminating the need for oil scrubbing of the recycle, as the diluents were largely removed in the vapor-phase oils. Oils containing nitrogen and oxygen, not suited for 250- to 300-atmosphere operation, could be processed in a single step. Two 700-atmosphere plants were put in operation during the war processing tar-distillation and hydrogenation oils; one plant employed the tungsten sulfide-on-Terrana catalyst and the other employed a newly developed Mo-Cr-Zn-on-Terrana aromatizing catalyst.

During industrialization of coal hydrogenation in Germany, interest in other countries was intense. Wiley and Anderson (65) cited 2,503 articles and 3,569 patents on the subject. Extensive experimentation was conducted to expand the knowledge of the art and to determine the amenability of coals to hydrogenation. Excellent reviews (26, 27, 54, 69) and critical discussions (28, 56, 57) in the literature reflect this research. A brief generalized summation follows.

Numerous investigations and results from German industrial operations established that the reactivity or amenability of coals to hydrogenation is approximately inversely related to their carbon content. The lower rank coals hydrogenate with greater ease, at lower pressures and temperatures, and with catalysts of lower activity. As their carbon content increases, coals become increasingly more difficult to hydrogenate; coals with a moisture- and ash-free (m.a.f.) carbon content above 86 percent have been considered unsuitable for hydrogenation. For a given rank, coal type affects reactivity; anthracite is liquefied almost completely under normal hydrogenation conditions; bituminous is affected very little; and lignite and subbituminous occupy intermediate positions. Thus bright coals of higher rank may hydrogenate more readily than dull coals of lower rank.

Probably the first stage in coal hydrogenation is depolymerization of the coal molecule and colloidal dispersal of the degraded molecules in the vehicle oil. Virtually complete solution of some coals in anthracene oil is possible, and all coals below anthracite can be substantially dispersed even in the absence of hydrogen. Hydroaromatics of condensed ring structure containing phenolic groups appear to be the most effective media. It has been postulated that readily dehydrogenated oils serve as hydrogen donors to the depolymerized coal molecule. For each coal tested there is an optimum solubilizing temperature above which repolymerization and precipitation occur. Appreciable hydrogen pressure permits higher temperatures and results in more complete solubilization.

Studies of restricted hydrogenolysis indicated that the first products formed (as a result of the initial depolymerization and the removal of most of the oxygen, half of the nitrogen, and substantial amounts of the sulfur) are tarlike in nature. Hydrogenation proceeds apparently by progressive degradation-hydrogenation of the molecule, opposed by a concurrent repolymerization reaction, with time-temperature-catalyst-pressure relationships determining the direction and extent of the reactions. Higher temperatures accelerate all the reactions, but an increase in temperature above the optimum for

the system tends toward formation of gaseous hydrocarbons and cokelike polymers. An increase in catalyst concentration and hydrogen pressure accelerates the reactions with hydrogen and suppresses repolymerization. Thus, an active catalyst and high hydrogen pressure permit operation at somewhat higher temperatures, the extent of degradation to light hydrocarbons being controlled by reduction in reaction time.

Despite intensive catalyst research, coal hydrogenation remained essentially a high-pressure process. Tin as stannous chloride or tin oxalate was very effective in the liquefaction of coal, particularly with addition of small amounts of volatile halides. The use of tin permitted hydrogenation of bituminous coal at 250-300 atmospheres pressure. Ammonium molybdate impregnated on the coal was equally effective, and, like tin, was active in very small concentrations. Lower rank coals were successfully hydrogenated at these lower pressures with bog iron or with Bayermasse (a crude iron oxide byproduct from aluminum manufacture). Bayermasse plus ferrous sulfate was utilized with (higher rank) bituminous coal at 700 atmospheres pressure.

The role of pasting oil in primary liquefaction had been variously investigated. Besides being a vehicle for coal and coal solids, it was found that it served probably as a hydrogen-transfer medium, increasing the reaction velocity of coal by its presence and thus lowering catalyst requirements.

In vapor-phase hydrogenation many materials had been tried as catalysts, but none had been found more strongly hydrogenating than molybdenum and tungsten disulfides. Tungsten, the more active of the two, excelled for saturation and was effective as a splitting and isomerizing catalyst, but produced a relatively saturated, mediocre gasoline. Use of a supported catalyst overcame these deficiencies; 10 percent tungsten on activated Terrana produced a catalyst that was more weakly hydrogenating but equally active for splitting and better for isomerizing. However, this catalyst was sensitive to oxygen and nitrogen in the oils, requiring prerefining or saturation of oils having a high content of these substances. At higher temperatures this supported catalyst was effective in the production of aromatic gasolines. More active aromatizing catalysts were based on activated charcoal impregnated with iron and tungsten or chromium and vanadium oxides. More efficient catalysts, consisting of Zn-Cr-Mo on Terrana, were developed later for operation at 700 atmospheres.

The bulk of research was directed toward improvement and refinement of the Bergius-I.G. Farben. process. On a pilot-plant scale in England the effect of turbulence and temperatures up to 1,100° F. had been investigated in a tubular reactor. The Pott-Broche process, wherein a tetralin-cresol coal extract was hydrogenated, reached the commercial stage in Germany. Two other variants of the conventional process were developed in France to the semi-works scale. The first variant liquid-phase reactor used tubes in bundles, set in a coke-oven-like structure, through which the coal paste and hydrogen were passed; the second employed a tower resembling a plate fractionation column, in which hydrogenation residues were subjected to increasingly higher temperatures as they flowed down the column. Dry-coal hydrogenation (without vehicle oil) had been carried out in autoclave experiments in Germany; good

yield of oil and production of a dry char from brown coal at low pressures (25 to 50 atmospheres) indicated the desirability of further development.

Bureau of Mines Contributions to Coal Hydrogenation, 1944-55

The chemistry of coal hydrogenation is quite complex, and the engineering problems involved in its application are difficult. Development of high-pressure and high-temperature equipment for continuous operation, as required to evaluate and to improve existing techniques, and to explore the feasibility of new approaches suggested by basic studies, was studied by the Bureau of Mines, largely in the laboratories at Bruceton, Pa. Process variables and catalysts were studied with various ranks of coal. Low-pressure hydrogenation, high-temperature hydrogenation, and hydrocarbonization were also investigated. A limited amount of vapor-phase catalyst testing has been completed. Continuous hydrogenation of raw shale oil and of a coker-distillate shale oil have been evaluated. Techniques for the removal of solids have been investigated.

Meanwhile, more basic problems that were attacked included studies of coal structure, reaction mechanisms, the role of catalysts, identification of the complex reaction products, and the effect of the many important reaction variables. In this work modern techniques, such as the infrared, mass, X-ray, and diffraction spectrograph, have been utilized to the maximum extent.

Basic Research

Fundamental studies have been performed on the structure, chemistry, and microbiology of coal. These studies are expected to contribute toward our knowledge of the origin and structure of coal and to help in explaining the behavior of coal in chemical reactions. Such basic knowledge may also suggest new possibilities in the development of processes that start with coal as the raw material.

Physical Studies on Structure of Coal

Sorption Studies on Coal. - Research of the British Coal Utilisation Research Association, beginning about 1940, and of workers in South Africa and The Netherlands, contributed valuable experimental data and interpretations on sorption phenomena. However, interpretation of these data has led to still unresolved arguments. The controversy has to do with interpretation of observations that (1) sorption of inert molecules such as argon and nitrogen at liquid nitrogen temperatures is relatively low, corresponding to surface areas of 0.5 to 15 m.² per gram, while (2) the sorption of polar molecules such as alcohols and amines at room temperatures is high, corresponding to surface areas of 50 to 400 m.² per gram. The British group believed that the areas calculated from sorption of polar molecules, especially methanol, were correct and that sorption of inert nonpolar molecules on coal was prevented by methane in the pores and by the slow rate of diffusion. Others (41) suggested that the sorption of inert molecules yielded correct areas, and that the greater sorption of polar molecules resulted from a weak chemical bonding with the coal.

Sorption studies on American coals (1) yielded similar data. The sorption of nitrogen at liquid-nitrogen temperatures was low on all coal samples examined, and sorption of methanol and water was much greater. Helium and mercury density measurements showed sizable pore volumes for several American coals.

For most of the coals, sorption of n-butane was found considerably greater than sorption of isobutane. From the sizes of the molecules it appears that n-butane could enter pores with openings larger than 4.9 A. units, whereas isobutane would require pores larger than 5.6 A. Therefore many of the pores in coal have openings of about 5 A. units.

On most American coals the sorption of nitrogen at -78° C. is significantly greater than at -195° C. As the amount adsorbed usually decreases sharply with temperature, the present results indicate that at lower temperatures sorption is limited by a temperature-dependent rate process (probably activated diffusion in pores) so that at the lower temperature the sorption in pores occurs only to a slight extent in a finite time. Sorption involving activated diffusion has been observed on materials (such as partly dehydrated chabazite) which contain pores that approach molecular dimensions. Like most American coals, this material also selectively adsorbs straight-chain hydrocarbons.

These studies indicate that coals have a sizable pore volume but that a large fraction of the pore volume has openings of about 5 A. At the temperature of liquid nitrogen, inert molecules such as nitrogen and argon are apparently adsorbed only in larger pores and do not enter the micropore structure of the coal. Surface area computed from these values is, then, the area of the portions of coal having large pore openings and is less than the "true surface area." Sorption of polar molecules such as water, methanol, methylamine, and ethylenediamine appears to involve weak chemical interactions with polar groups of the coal, and swelling of the coal substances. Surface areas computed from sorption of polar molecules are probably much higher than would be obtained if absorption did not occur.

Spectroscopic, X-Ray Diffraction, and Magnetic Resonance Studies of Coal. - Infrared spectra of many coal samples were examined to study the chemical composition of coal and similar substances (30, 32). Spectra were the same for bituminous anthraxylons of the same rank from various parts of the world, while those of different rank produced slightly different spectra. Spectra of natural asphaltic substances, such as petroleum asphalt and gilsonite, were generally similar to those of coal. The differences indicated quantitative but not qualitative variations in chemical structures. Several structural assignments were made, as shown in figure 39.

Spectral changes in residues, obtained by thermal degradation of bituminous anthraxylon in vacuum, were shown to parallel those observed with anthraxylons of different rank. The apparent rank increased with increasing temperature of degradation. Continuous absorption of visible radiation extended progressively farther into the infrared region as the temperature was raised. This change was attributed to increased amounts of π -electrons but not to formation of discrete condensed polynuclear aromatic systems.

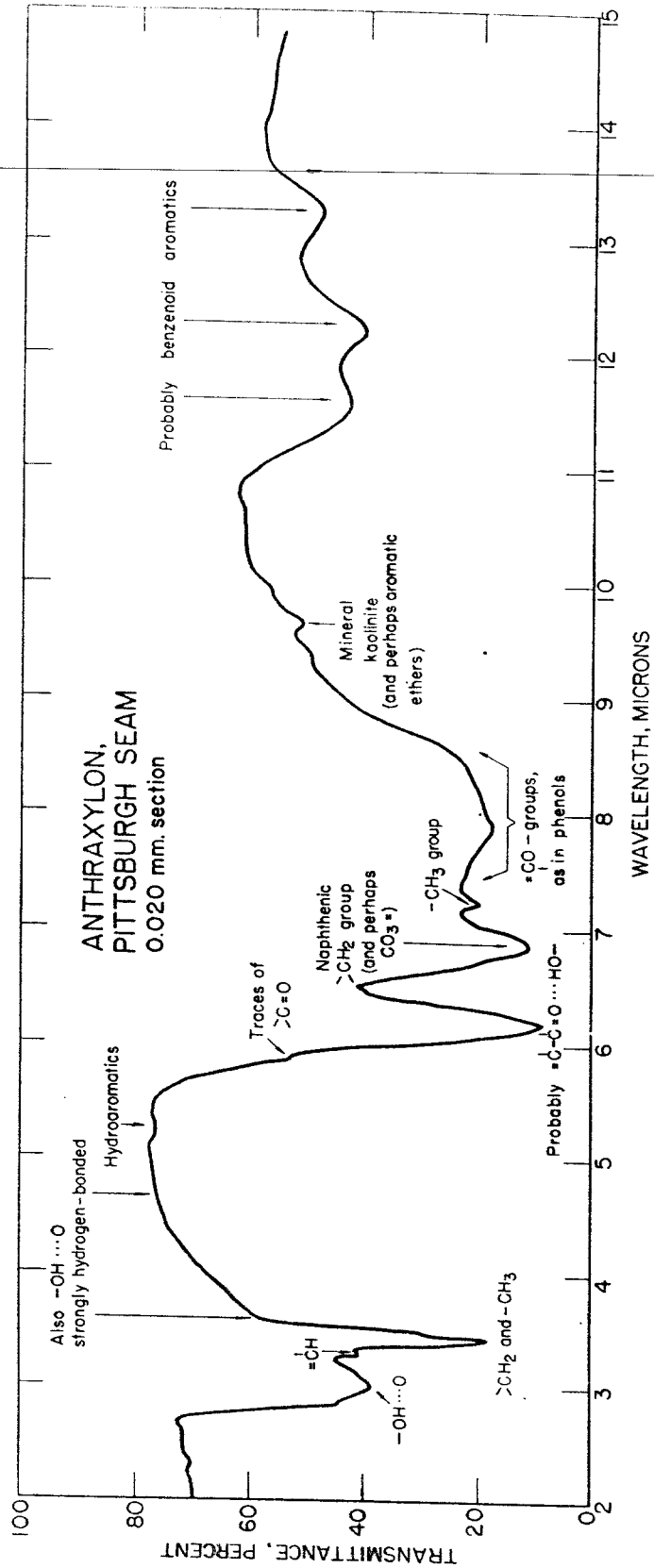


FIGURE 39. - Infrared Spectrum of Anthraxylon From Pittsburgh-Seam Coal; Assignments of Bands to Molecular Structures.