

7. Sump Phase Solids Removal and Oil Recovery (b)(cont'd.)

in the screw-type furnace, 3.2 tons as compared with 2 tons per hour. Another big difference was the much lower oil content in the residue, about 1-2 percent as compared with 20-25 percent. The higher temperature produced more gas so that the overall oil recovery was essentially the same. It was of interest, however, that the ratio of heavy oil to light oil was greater in the ball oven than in the screw type, despite the fact that the gas yield was almost double. The ratios of heavy to light oils were 4.8 and 3.4, respectively, from the two units operating on the same feed.

Table No. 8 in Appendix A contrasts the operation of these two types of furnaces.

8. Description of the T.T.H. Process.

The T.T.H. process or Tief Temperatur Hydrierung (low temperature hydrogenation) represented a markedly different approach to the hydrogenation of coal tar to obtain diesel fuel and lubricating oils. In 1935 experimental work was started on the problem of preparing lube oils from brown coal tar by means of a limited hydrogenation so as not to destroy the paraffinic nature of the tar. By 1938 the work had reached the stage for commercial application, and in 1939 the first and only plant in Germany was started at Zeitz.

The feed for the process consisted chiefly of brown coal tar from low temperature carbonization with about 10 percent of light oil added. The raw tar contained about 0.5 percent finely suspended dirt and 0.4 percent water which were largely removed by centrifuging. The clarified tar was next filtered and the dirt content reduced to a maximum of about 0.01 percent. An analysis of the tar feed showed that it contained 33.4 percent carbon, 10.5 percent hydrogen, 2.0 percent sulfur, 0.4 percent nitrogen, and 3.7 percent oxygen. The specific gravity at 50°C was about 0.95, and analytical distillation showed that 6 percent boiled up to 180°C, 33 percent up to 325°C, and 52 percent up to 350°C.

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8. Description of the T.T.H. Process. (cont'd.)

The equipment in which the conversion was conducted was essentially the same as that used in the gas phase hydrogenation. The hot equipment was located in a stall which held two heat exchangers, an electric preheater and three catalytic converters. The Zeitz plant had five of these stalls operating on the T.T.H. process during the war. Since the equipment was nearly the same as that previously described, only those items which were different will be discussed.

The reaction occurred in the liquid phase over an active catalyst at between 300 and 390°C. under a total pressure of 300 atmospheres. A partial pressure of hydrogen of about 85 percent was maintained at the converter inlet, but at the outlet it had dropped to about 80 percent. The through-puts were relatively low averaging 0.35 and 0.4 tons of tar per cubic meter of catalyst per hour. In a three converter system having 25 cubic meters of catalyst, the tar through-put was therefore about 9-10 tons per hour. Approximately 25,000 cubic meters of gas per hour were mixed with the tar and heated in the exchangers and preheaters, while an additional 14,000 cubic meters were required for temperature control in the converters. The hydrogen consumption was approximately 550 cubic meters per ton of tar.

A hot separator was not used in this system, even though it was a liquid phase process since there were no solids to be removed. The whole product was collected in the cold catch pot and distilled.

The converter design was a little different from that employed in the gas phase, although the general features were similar. (See drawing no. C-14 in Appendix C). A forging 1000 millimeters in diameter by 18 meters long was insulated and lined as was done with both the sump and gas phase reactors. Only one grating, similar to that used in the gas phase converter was installed in the lower section so that the catalyst bed was continuous instead of being divided into sections. The catalyst volume was increased to 8.4 cubic meters by this means. It was still necessary to introduce cooling gas to control the reaction temperature,

8. Description of the T.T.H. Process. (cont'd.)

so six down pipes located at strategic points were used. A ring with holes around the circumference was connected to the lower end of each of the cooling gas pipes and used to distribute the gas throughout the catalyst bed. As in the gas phase reactors the thermocouple well was located in the center.

A rising flow of oil and gas were employed in the converters, since the velocities were not as great as in the other hydrogenation processes and the liquid phase tended to cushion the catalyst and reduce attrition. The catalyst most frequently used, when available, was no. 5058 tungsten disulfide pellets, the same as used in prehydrogenation. The complete preparation of this material is given in Appendix B. When tungsten became scarce, the substitute catalyst No. 7846W250, sometimes referred to as 8376, was used. This latter material was a mixture of 25 percent tungsten sulfide plus 3 percent nickel sulfide on activated alumina. As mentioned in Section V under the prehydrogenation process, this catalyst was very active in reducing oxygen and nitrogen compounds as well as hydrogenating the lower boiling constituents, but it was less effective in cracking and hydrogenating higher boiling materials. The milder cracking was desirable, but the reduced hydrogenation activating was a liability, so that altogether the Germans felt that 5058 catalyst was the better material to use whenever available.

The average catalyst life depended very greatly upon the purification of the feed tar. As previously explained, the dirt content was reduced to about 0.01 percent by centrifuging and filtration, and great care had to be exercised to keep this dirt value low. This suspended solid matter would gradually foul the catalyst surface together with condensed polymerization products that could not be desorbed. Soluble ash, such as iron phenolate, also caused trouble by being reduced and deposited on the catalyst surface. The only way to avoid the latter difficulty was to choose feed tars that contained very little soluble inorganic compounds. If proper precautions were taken, a catalyst life of six months to one year was obtained. Regeneration of the catalyst in situ was not possible, but instead fresh material was charged,

8. Description of the T.T.H. Process. (cont'd.)

and the active ingredients recovered at the catalyst plant.

The purpose of the process was to very carefully refine the high molecular weight paraffinic substances without cracking and destroying them, so that they could be recovered as lube oils and waxes. For this reason the low temperature was absolutely necessary, as the lube oil fraction decreased rapidly above 390°C and at 420°C it practically disappeared being converted into gasoline and diesel oil. Under actual condition approximately 80 percent of the fresh tar was converted into desired products with the following distribution: 27 percent gasoline, 43 percent diesel oil, 5 percent lube oil, 9 percent wax, 0.5 percent C₃ + C₄ gas, and 14 percent residue which could be processed in a sump phase tar hydrogenation plant.

The gasoline, as produced, was not useable directly, but had to be further treated in either the gas phase plant or in a DHD process. Its average composition was 5 percent aromatics, 30 percent naphthenes, and 65 percent paraffins, and consequently the octane rating was low, about 55. The diesel oil fraction boiled from 200 to 320°C and had a cetane rating of 45-50. Its composition was similar to that of the gasoline, but it was a satisfactory fuel as produced, whereas the gasoline was not. The phenol and sulfur contents averaged 1 percent and 0.1 percent, respectively.

After removing the gasoline and diesel oil cuts, the residue oil was vacuum distilled to produce lube oils. The total lube oil fraction had a VI of 60 to 80, but it was usually fractionated to produce a spindle oil and a machine oil. The relative yields were approximately two-thirds of 4° Engler spindle oil and one-third of 6 to 8° Engler machine oil.

The waxes were extracted from the residue by means of the conventional propane process. These were divided into soft and hard wax. The former constituted about one-third of the product with a melting point of 40-45°C; the latter two-thirds with a melting point of 52°C. These waxes were used for the production of fatty acids, or were cracked

8. Description of the T.T.H. Process. (cont'd.)

and the olefines polymerized to make lubricating oils.

A complete report of the operation of the T.T.H. process including actual yields for 1944 at the Zeitz plant was obtained, and further information on the process, if desired, may be obtained from this document. (27)

9. Description of Pott-Broche Process.

Although this method for treating coal was more like a solvent extraction than a hydrogenation, however, its similarity in operating conditions and its use in conjunction with coal hydrogenation plants makes this report the logical place for presentation. Briefly, the theory of the operation was to contact finely ground coal with a suitable solvent at a temperature and pressure high enough to dissolve a major portion of the coal. The untreated coal and ash were removed by filtration and the solvent recovered by distillation leaving a high molecular weight coal extract which could be fed to a coal hydrogenation plant to produce fuels.

In 1927 research work on the commercial application of solvent extraction to bituminous coals was started by Drs. Pott and Broche. The work progressed slowly, but by 1934 it had reached the point where it was deemed advisable to build a pilot plant for testing the process on a larger scale. In 1936 the Ruhrol A.G. constructed the first commercial unit with a capacity of 26,000 tons per year of bituminous coal extract. On account of difficulties and peculiarities in the process, which will be discussed later, this was the only plant built and operated in Germany for coal extraction.

The feed material was Ruhr bituminous coal which had a moisture content of 5-10 percent and an ash content of 5-7 percent. On a dry, ash-free basis the coal contained 86.7 percent carbon, 5.1 percent hydrogen, 1.2 percent sulfur, 1.6 percent nitrogen, and 5.4 percent oxygen. The volatile matter content averaged 27-28 percent, which was...