

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...

9. Description of Pott-Broche Process (cont'd.)

markedly lower than the 38 percent obtained from bituminous coals used in nearby hydrogenation plants. The coal was dried to 0.5 to 1.0 percent moisture content, and then ground in ball mills so that 95 percent was finer than 100 mesh, and about 65 percent was finer than 250 mesh. See drawing no. 3 for process flows.

The coal was next mixed at about 90°C with twice its weight of solvent in large steam-heated, agitated tanks. The solvent originally used was a mixture of 80 percent tetralin and 20 percent cresols, while the newer operation was to use a sump phase middle oil which was rich in these materials. After the coal had been thoroughly suspended in the oil, the paste was pumped to the extraction apparatus. This consisted of a preheater and an extraction section mounted in a single furnace. A gas-fired furnace similar in construction only larger, than those employed as preheaters in the coal hydrogenation plants, was used to heat 48 hairpin tubes approximately 15 meters long. The first 24 tubes were finned exactly like the hydrogenation plant preheater tubes and served to bring the materials up to reaction temperature. The last 24 tubes, which were slightly smaller, did not have fins and these served as the extraction chamber. All of the tubes were connected in series with the preheat section forming a circle around the outside of the reaction section. The rest of the construction was standard practice such as the use of hot recycle flue gas blowers and lens ring joint connections between "U" bends.

The average through-put of the unit was 16 tons per hour of which 5.3 tons was coal. The temperature at which the solution of the coal occurred rapidly was about 420-430°C and the pressure 100 to 150 atmospheres. Since this process was operated without the addition of gaseous hydrogen, the maximum temperature was lower than that employed in coal hydrogenation plants; the operating conditions being a compromise between rate of reaction and coking of the contents. After one hour contact time in the tubes, about 75 percent of the ash-free coal was dissolved in the solvent, the residue consisting of refractory

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DRAWING No. 8

(This drawing has been inserted in an envelope  
attached at the end of this report)

9. Description of Pott-Broche Process (cont'd.)

bitumens and fusain.

The theory of the action of the solvent was that under the influence of heat and catalyzed by the cresols, the coal was depolymerized. The four loosely-bound hydrogen atoms in the tetralin were available to stabilize the decomposition products and prevent them from repolymerizing into higher molecular weight cokes. The tetralin, therefore, acted as a donor of hydrogen; or stated in another way, the use of tetralin provided a means of introducing hydrogen into the system without the use of gaseous materials. Naphthene and paraffin type compounds, such as decalin or decane, were entirely unsuited since the hydrogen atoms were too tightly bound to be available for hydrogenating the depolymerized coal substances.

In the original process the tetralin would be nearly all converted to naphthalene during the reaction, and consequently it was necessary to use another step to hydrogenate the naphthalene back to tetralin before it could be used again in the extraction. The newer practice took advantage of the proximity of the adjacent pitch hydrogenation plant and the fact that the sump phase middle oil contained a large percentage of partially hydrogenated aromatics as well as phenolics. Therefore, it was possible to substitute sump phase middle oil for the tetralin-cresol mixture, and thus simplify operation. The recovered solvent was then processed in the gas phase hydrogenation unit, and interestingly enough the octane rating of the gasoline was raised. The exact cause for the latter effect was not known, but it appeared to be connected with an increased aromatics content.

The slurry of coal solution and solids after leaving the reaction chamber was filtered to remove the solids. Three ceramic cartridge filters containing about 35 elements each were employed to filter the slurry at 1500C and six atmospheres differential pressure. The filter medium was a porous stone annular ring, about 125 by 80 millimeters in diameter by 33 millimeters thick. Approximately 60 of these were mounted on tubes, and so arranged in the filter

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### 9. Description of Pott-Broche Process (cont'd.)

that the oil passed through the stone into the inner hollow section and was then collected in filtrate tanks. The solids were collected on the outside of the ceramic cartridge, and after about 13 tons of slurry had been filtered, the cake was discharged by carbon dioxide introduced inside of the element. The filters worked reasonably well, and about 4000 batches could be handled before the mediums became so dirty that they had to be replaced.

The ash and solid free solution was next vacuum distilled at 50 to 100 millimeters to recover the solvent. The residue, which amounted to 3.7 tons per hour, was a high molecular weight material that resembled asphalt in appearance. It had a melting point of about 200° C. and a volatile matter content of 40-42 percent. The ultimate analysis of the extract averaged 89.2 percent carbon, 5.3 percent hydrogen, 1.5 percent nitrogen, 1.1 percent sulfur, and 2.9 percent oxygen, while the ash content was reduced to about 0.05 percent. This extract was the primary product of the process, and it was further treated as well be described later.

The heads fraction from the vacuum distillation was again distilled at atmospheric pressure to give recycle solvent with an F.P. of 220°C, and a residue that was sent to the sump phase for hydrogenation. Part of the solvent recovered was sent to the gas phase hydrogenation plant, while the rest was mixed with fresh sump phase middle oil and used for pasting coal.

The filter cake containing about 65 percent oil by weight, was coked in a rotary kiln at about 400°C to recover the oil. The solid residue was either mixed with coal and burned or discarded, as it was very difficult to ignite and had a low heating value on account of its high ash content.

The original intention of the Ruhröl Company had been to use the coal extract in the sump phase process to make synthetic fuels. It was an easier material to handle than coal on account of the absence of ash and materials very difficult to hydrogenate. However, it was not as readily

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9. Description of Pott-Froche Process (cont'd.)

processed as tar or pitch which were further along the path toward middle oil. Since Germany required the maximum production of gasoline from each plant, it was more expedient to process pitch than coal extract. Therefore, the extraction process was not operated to produce stocks for hydrogenation, but rather for special purposes. It was found that the extract could be coked to give a carbon that made good electrodes for use in the aluminum industry, and hence most of the production was diverted to this purpose. The Ruhröl Company felt that the future of the process lay in the production of special purpose materials rather than in the manufacture of motor fuel. They felt that the extract might be used as molding plastics, fillers in structural material, or as insulating coatings for wires and cables. In order to dissolve the extract a solution of cresol, tetralin, benzol, and pyridine was used since ordinary solvents were not suitable. This process may find greater commercial application in the future, although to date its record has not been very impressive.

10. Discussion of the Products of Hydrogenation.

As has been described in the previous sections of this report the Germans made a variety of synthetic fuels by hydrogenation of coals, tars and pitches, but each of the raw materials had its own characteristics which made it a better stock for certain products than for others. This section of the report, therefore, is an endeavor to rationalize the various hydrogenation processes and contrast the variations in the products. Although the German fuel program for the war was a complicated series of balances, yet there were several general principles which governed the production program, and this section will attempt to show how these operated.

All of the five main sources of raw material, namely brown coal, brown coal tar, bituminous coal, bituminous coal tar, and pitches plus cracking residues, could be treated to produce various yields of aviation grade gasoline. There were three main ways of preparing aviation gasoline, namely,