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3. General Outline of Hydrogenation (cont'd.)

of the operators of this process was that it was better adapted for making special products such as coatings and insulation, than for fuels.

The various steps of the coal hydrogenation processes are discussed in greater detail in sections 4 to 9 inclusive, and in section 10 comparisons of the products and operation of the different methods are presented.

4. Description of Sump Phase Operations.

(a) Processing of Brown Coal.

The German brown coal or lignite occurred in large thick beds, which averaged 200 to 300 feet in depth. On account of the thickness and proximity of these beds to the surface, strip mining methods were employed. The brown coal as mined resembled dirt in appearance, since it had a deep chocolate color. The coal preparation, which included drying, grinding, and paste mixing, are discussed in detail in U.S. Naval Technical Mission in Europe Report entitled "Production of Hydrogen and Synthesis Gas from Solid and Gaseous Fuels" (9), and hence only the principal points will be described here.

The raw lignite contained on the average 50 percent moisture content before use. The brown coal when dry was very susceptible to spontaneous combustion in air, and consequently, elaborate precautions were taken to keep an inert atmosphere of carbon dioxide or nitrogen over the coal at all times during the drying, grinding, and pasting. The pulverizing of the coal was accomplished by mixing heavy recycle oil from the centrifuges with dried coal in ball or mixing mills and wet grinding until the coal had been properly comminuted and a homogeneous suspension of coal in oil, known as paste, produced. For best results the oil had a viscosity of 100-150 centistokes at 85°C., and sufficient coal was added to give a paste that had a viscosity of 1500-2000 centistokes at 85°C. Although the viscosities were measured at 85°C., the actual operating temperature of the mills was usually about 120°C, since this reduced the vis-

4. Description of Sump Phase Operations (a)(cont'd.)

cosity of the oil and permitted most of the free water in the coal to be vaporized.

The concentration of coal in the resultant paste depended upon several variables such as the type of coal and the quality of the pasting oil. The Wesseling plant, which processed Rhine lignite(10), could only handle 36 percent coal in the feed on account of the "gelation" properties, whereas Leuna which treated middle German lignite, operated with 40-42 percent coal in the paste. The average weight of the coal paste was 1.1 tons per cubic meter.

During the grinding of the coal in the oil, catalysts were added and thoroughly mixed in the paste. Iron and sulfur were the more common catalytic elements used for brown coal hydrogenation, and since most coals contained 3 to 6 percent sulfur, it was usually only necessary to add iron. This was accomplished by the addition of 4-6 percent, based on the weight of coal, of "Bayermasse" or "Roterz" (impure iron oxides produced during the purification of alumina ores.). With the Rhine coal, which was very low in sulfur (0.75 percent), it was necessary to add about 1.25 percent of elementary sulfur to the paste, but in other plants this was not necessary(10). Molybdenum and/or zinc had previously been used for catalysts, but iron and sulfur were nearly as active and had the advantage of being much cheaper.

The coal was ground so that about 40 percent was finer than 250 mesh (English measure) and essentially all of it was under 200 mesh before it left the mill. The paste was fed to the large high pressure paste presses in a recycle system which kept the feed moving throughout the entire manifold, and assured a continuous supply of hot uniform composition paste to each of the several pumps connected in parallel. The paste presses were large, double-acting, hydraulically driven piston pumps, which had capacities varying from 10 to 25 cubic meters per hour maximum, depending upon the different sizes employed at the various plants. In general, the larger capacity pumps were newer; the smaller sizes being old machines still kept in service. In order

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4. Description of Sump Phase Operations (a)(cont'd.)

to better resist the abrasive action of the coal paste, the plungers were hardened to about 400 Brinell, and the valve seats were made of specially hardened alloy steel. The packing material was usually metallic rings of either white metal or lead-calcium alloy, and a lantern ring was located in the packing section so that between 80 and 200 liters per hour of flushing oil could be injected to keep paste out of the stuffing box. By the use of flushing oil the packings had a life of about six months under normal operating conditions.

The paste leaving the presses at either 300 or 700 atmospheres depending upon the method of operation, as will be described later, was joined with recycle gas and entered the first heat exchanger in the coal stall. All of the coal hydrogenation plants were constructed on the basis of individual coal stalls or chambers, and each chamber contained two heat exchangers, one preheated, three or four converters, and a hot separator. These pieces of apparatus were mounted in a tall concrete structure which helped to protect the operators by isolating the equipment and localizing fires that might occur from mechanical failures. The size of the various plants depended upon the number of stalls which they operated, since the output of any one stall did not vary greatly among the various plants. Large plants, such as Leuna, operated nine (9) sump phase stalls, whereas the smaller installations usually consisted of two to four units.

The heat exchangers were large forgings of chrome-nickel molybdenum steel 500 or 600 millimeters inside diameter by 18 meters long; the two sizes differed only in the number of tubes and consequent available heat transfer areas. Inside of the steel forging was a diatomite or brick lining about 65 millimeters thick which insulated the pressure wall from the hot contents. A thin stainless steel tube (0.5mm) was located inside of the insulation, and this liner contained the fluid products and resisted the corrosive attacks of high temperature hydrogen and sulfur. The tube bundle with baffles was placed inside of the liner, and connected to the heads through conical adapters. The tubes were made of galvanized N5 steel (chrome-vanadium

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4. Description of Sump Phase Operations (a)(cont'd.)

alloy) and measured 23 by 14 millimeters by 16.5 meters long. The 500 millimeter heat exchanger usually held 151 of these tubes and had a heat transfer area of 145 square meters, whereas the 600 millimeter exchanger had 199 tubes and 190 square meters of surface. The closures were made by the compression of aluminum gaskets in the conventional manner, by bolts on each flanged head. The assembly and construction details are shown in drawing no C-1 in Appendix C.

In operation the paste and gas entered at the bottom of the first heat exchanger at about 60 to 80°C, and flowed up around the outside of the tubes, counter-current to the outlet products inside of the tubes. The paste leaving the first exchanger had been heated up to about 200°C, and it then was further heated in a similar manner in the second unit to about 320°C. (Refer to drawing No. 2 for flows in the sump phase). The heat transfer coefficients varied greatly, as would be expected with materials that fouled and corroded the equipment, and hence the average values were difficult to determine. For equipment in good condition, the overall heat transfer coefficient varied from 200 to 250 kilocalories per hour per square meter per degree centigrade (40-50 BTU per hour per square foot per degree Fahrenheit). After the surface had become fouled from caking or coking of solids, the values might drop to 50-100, at which time it was usually necessary to take the equipment out of service(11,29,30).

After leaving the second heat exchanger, the feed entered a gas-fired preheater where its temperature was raised to about 410-430°C. The preheater was a rectangular furnace about 7 meters long by 4 meters wide by 14 meters high, divided into sections to hold the preheater tubes. Drawing Nos. C-1 and C-2 in Appendix C shows one of the more common types of gas-fired heaters, in which hair pin tubes were located in vertical rectangular sections at one end, and the combustion chamber was at the other end. Fuel gas was burned in the combustion chamber, and the hot gases mixed with hot recycle gas and passed through the sections housing the preheater tubes counter-current to the flow of material being heated. The gas leaving the last tube

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DRAWING No. 2

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attached at the end of this report)

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4. Description of Sump Phase Operations (a) (cont'd.)

section was picked up by recycle blowers and returned to the mixing chamber. This high circulatory system, using two blowers of 50,000 cubic meters per hour each (measured at 1 atm. and 450°C) helped to prevent local overheating and increased the thermal efficiency. The heating value of the fuel gas employed was about 2000 kilo calories per cubic meter, and between 3000-4000 cubic meters per hour were required. (12)

The hair pin tubes were constructed of N8 or N10 steel, which were chrome, vanadium, molybdenum, tungsten alloys of high tensile and creep strengths. The tubes themselves were 171 by 120 millimeters in diameter, and about 14 meters long. The number of tubes required varied greatly from plant to plant, the range being from 6 to 20 hairpins. In any case the principle of operation was the same, and the furnace was proportioned to accommodate the number of tubes required. On the outside of the tubes, perpendicular to the central axis, were welded a series of steel fins 300 millimeters square, four millimeters thick, and spaced 14 millimeters apart. These fins added heating surface, and thus raised the heat transfer rate which nevertheless was very low. The heat transfer coefficient averaged 6-8 kilo calories per hour per square meter per degree centigrade.

After leaving the preheater, the hot paste-gas mixture entered the first of a series of three or four converters. The older designs used three vessels, whereas the more modern practice was to use four, and hence this report will discuss the four converter coal stall. Three very common sizes of converters were used, either singly or in combination with each other; however, the only important differences, between them were the overall dimensions, since the internal construction was essentially the same. The details of the construction are shown on drawing no. C-4 in Appendix C. Two of the converters were 800 and 1000 millimeters inside diameters, respectively, by 18 meters long, while the third was 1200 millimeters by 12 meters long. The pressure bodies were forgings of N2 (chrome-molybdenum) steel, heat treated to improve the mechanical strength. The inside surface was insulated with two layers of diatomite brick and

4. Description of Sump Phase Operations (a)(cont'd.)

asbestos cement so that the thickness of the insulation was about 65 millimeters. A thin V2A (stainless) steel liner, about 0.5 millimeters thick, was placed inside the insulation and connected with the top and bottom heads through conical adapters. The stainless steel liner was used to contain the reactants, since it was resistant to sulfur and hydrogen corrosion. The closures were of the straight compression type, as in the case of the heat exchangers using aluminum gaskets, since copper would have been corroded by the sulfur and ammonia. In the top head were three or four small inlet connections for introducing cold hydrogen at different points in the converter to control the reaction. A large inlet and outlet connection were located in the center of the bottom and top heads, respectively, and the external piping was connected by means of standard lens ring type points.

The hydrogenation of coal is an extremely complicated chemical process, and since coal is not a homogeneous substance, but is composed of many high molecular weight organic compounds, it is impossible to state exactly what occurred during the reaction period. An average analysis of brown coal on a dry basis was 62 percent carbon, 5 percent hydrogen, 1 percent nitrogen, 5 percent sulfur, 18 percent oxygen, and 9 percent ash. The relatively high ratio of hydrogen to carbon, plus the high oxygen content, made the lignites reasonably easy materials to hydrogenate. On the other hand the high oxygen content caused a loss of valuable carbon which was eliminated as carbon dioxide, and also a hydrogen consumption to produce water. The brown coal apparently contained a large fraction of paraffin base substances with carboxylic acid groups, as well as condensed aromatic and naphthenic rings with oxygen, nitrogen, and sulfur included in the rings and in scattered connecting bridges. Under the action of heat and high hydrogen pressure, the large molecules were depolymerized with the loss of a large percentage of the oxygen as carbon oxides from the carboxylic acid groups, and as water from ether type linkages. Similarly part of the nitrogen and sulfur were eliminated as ammonia and hydrogen sulfide, respectively, while a fraction of the nitrogen remained in bases such as

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4. Description of Sump Phase Operations (a)(cont'd.)

aniline, and the oxygen and sulfur in phenols and thiophenols, respectively. A considerable amount of cracking and hydrogenation of the depolymerized coal oil resulted in the hydrogen content being markedly increased and the average molecular weight of the oil being lowered. During the reaction, part of the carbon in the coal was also converted into gaseous products ranging from methane to butane. Obviously, some of these reactions occurred simultaneously, while others went in series, but the principal overall effect was to convert most of the coal into a lower molecular weight oil having a hydrogen content higher than that of the original coal, and at the same time to form a considerable fraction of gaseous materials.

In the processing of brown coal a pressure of 300 atmospheres was sufficient to handle the middle German coals, such as Leuna used, but 700 atmospheres was needed to properly convert the more refractory Rhine lignites.⁽¹⁰⁾ These latter coals were poor in hydrogen and rich in oxygen, and by experiment were found to require the higher pressure. The overall conversion of the carbon in the coal to gaseous and liquid products was between 95 and 99 percent, but the oil yield was low because of the high oxygen content. It took approximately 2.1 tons of lignite to produce one ton of middle oil, so that the production per stall was not as great as when treating older coals or tars.

The hot paste and gas mixture leaving the preheater was joined by additional fresh hydrogen, heated in a separate set of "U" bends in the preheater, and then the combined feed entered the bottom of the first converter. The production of hydrogen for the process is described in detail in U. S. Navy Technical Mission in Europe Report entitled "Production of Hydrogen and Synthesis Gas from Solid and Gaseous Fuels" (9). Inside the converter the flow of gas carried a quantity of solids and heavy oil up the center of the vessel to the top, where the gas and part of the liquid products left the converter, and entered the base of the second reactor. Some of the solids and heavy oil, having a higher density than the average fluid contents, sank down the sides until they either reached

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4. Description of Sump Phase Operations (a)(cont'd.)

The bottom or were again trapped in the gas and carried toward the top. In this manner the contents of the converter were continuously circulated, thus providing better heat transfer and temperature control, as well as permitting the materials that needed hydrogenation most to remain the longest in the reaction zone. The first one or two converters were usually larger in diameter than the latter ones, since this permitted better circulation during the initial stages of the hydrogenation. For 300 atmosphere operation the 1200 millimeter diameter by 12 meter long converter was usually used first, while at 700 atmospheres the size was usually 1000 millimeters by 18 meters. The last converters in the series were usually 800 millimeters by 18 meters long.

The hydrogenation of coal was a highly exothermic reaction, and the feed was quickly heated up to the reaction temperature of 470-480°C within the first few meters of travel. The average through-put of paste was 1.1 to 1.3 tons per cubic meter of reaction space per hour, and for a four converter coal stall with 27 cubic meters reaction volume, this corresponded to 30-35 tons per hour. The corresponding gas flow was about 25 to 30,000 cubic meters of gas with a hydrogen content of about 80%. In order to control the temperature during the reaction due to the heat liberation of about 400 kilo calories per kilogram of coal, an additional 10-15,000 cubic meters of cold hydrogen were introduced through the connections on the top heads, into the converters at three or four levels. The turbulent cycle in the converters helped the heat transfer, and by adjusting the amount of hydrogen added, it was possible to control the temperature and prevent local overheating. The amount of gas circulated was several times that theoretically required, since only 1500 cubic meters of hydrogen were consumed in the production of one ton of middle oil.

The temperature was usually controlled by the asphalt content of the coal liquefaction products, since a high asphalt oil required a high temperature to give satisfactory conversions to lighter oils. The gas formation, partic-

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4. Description of Sump Phase Operations (a)(cont'd.)

ularly the methane, was greater as the temperature increased, so that it was desirable to operate it the lowest temperature consistent with a satisfactory reaction rate and conversion. Brown coals were usually low in asphalt, and hence high conversions and little trouble from this material were experienced.

One of the most troublesome problems with lignite was the formation of little solid balls of calcium carbonate which settled to the bottom of the converters and caused stoppages. These globules were called "caviar" or account of their resemblance to the real product, and means had to be supplied for their removal. (13,14) Usually the formation was most troublesome in the first converter where the coal was undergoing the initial decomposition. By means of a line tapping into the base of the first converter, a small amount of sludge, such as 100-200 liters per hour, could be withdrawn and treated in the solids removal unit. Usually only the first converter needed this simple sludge withdrawal line, but the plant at Wesseling had more difficulty with the Rhine brown coal, and more elaborate methods were needed to cope with the "caviar" problem. For more complete details on "caviar" refer to U.S. Naval Technical Mission in Europe Technical Report No. 87-45, pages 52-58. (15)

After passing through the converters in series, the gaseous and liquid products, together with a small amount of unconverted coal, ash, and catalyst, entered a large high pressure vessel called the hot separator. This apparatus performed a very important function besides merely separating the gases from the heavy oil and solids. Operating at a temperature of about 450°C, practically all of the water and a large fraction of the more volatile oil constituents were stripped from the solids containing heavy oil. This separation of a light overhead oil from the heavy oil was, of course, not as sharp as would be obtained by a distillation of the total product, but the fractionation of such a heavy oil containing solids would have presented formidable difficulties. Approximately 80 percent of the oil boiling up to 350°C was stripped from the heavy slurry by this process.

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4. Description of Sump Phase Operations (a)(cont'd.)

The hot separator was a vessel of NI (chrome-molybdenum) steel 800 millimeters inside diameter by 9 meters long. (See drawings nos. C-5 and C-6 in Appendix C. for details of construction) As in the converters and heat exchangers it was necessary to insulate the walls and use a stainless steel liner to hold the fluid contents. In the top head were inlet and outlet connections for the converter products, and gas plus oil vapors, respectively, as well as connections for a thermocouple well and liquid level regulator pipes. The lower head contained the outlet for the heavy oil plus solids. The inlet pipe was brought in and down one side of the vessel instead of being centered, since this apparently gave better separation of the gas and liquid products. The volume of the separator up to the feed down-pipe was approximately 1.5 cubic meters. In operation the liquid level was held reasonably constant by an automatically-operated liquid level controller.

There were several minor variations in design of the separator; the chief differences being in the inlet pipe and the bottom cone. One of the more common models employed a steep conical bottom connector to prevent solids from adhering to the wall of the liner, thus aiding in the removal of the solids from the separator. Cooling coils were inserted in both the top and bottom sections, and part of the fresh hydrogen for the process was given a little preheat here. By control of the quantity of cooling hydrogen, it was possible to regulate the amount of oil stripped out of the product, and hence the solids concentration and viscosity of the residual oil could be adjusted. In normal operation the solids content in the slurry was held between 20 and 25 percent.

The gas and oil vapors leaving the top of the separator passed down inside of the tubes of the second or hot heat exchanger countercurrent to the warmed paste and gas feed. With an inlet temperature of 430-450°C., the products were cooled to about 275°C, and then entered an intermediate separator to collect the condensed oil. This vessel was a forging of the same size and shape as the hot separator, but the internal apparatus was much simpler, since only

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4. Description of Sump Phase Operations (a) (cont'd.)

clean light materials were handled. The bottom head had a rather flat conical adapter, and there were no cooling coils employed. The condensed oil volume was controlled by a liquid level regulator connected to the apparatus.

The gaseous products leaving the intermediate separator next passed to the top of the first or cold heat exchanger. Frequently, it was necessary to add water to the gas stream at this point to prevent inorganic salts, such as ammonium carbonate and sulfide from condensing and causing crusts or stoppages. About 1000 liters per hour of water were usually sufficient, but with certain coals, such as Rheine brown, it was necessary to use so much as 2100 liters.⁽¹⁵⁾ The products were cooled in passing through the heat exchanger to between 175-200°C.

Further cooling was provided in trombone water coolers, which consisted of between 4 and 6 sets of 6 tubes each operating in parallel. The pipes were 58 millimeters inside diameter by about 16 meters long, so that the total surface was 80 to 120 square meters. Frequently, part or all of the previously mentioned water was injected at the inlet to the cooler, the difference depending upon plant operation.

The products leaving the cooler at about 70°C entered another large vessel known as the cold separator. This apparatus was a cylindrical forging usually 800 millimeters inside diameter by 6 to 9 meters long. See drawing no. C-7 in Appendix C., for details of construction. The ends were partly swedged so that the size of the openings into the vessel were about one-half of the inside diameter, and removable closures were used on each end. In operation the longitudinal axis was inclined at about 5 to 10° from the horizontal in order to provide a larger gas-liquid interface, and thus reduce the entrainment of froth in the outlet gas. The lower head had two connections, the upper one for the gas and liquid inlet, and the lower one for the liquid outlet. On the inside of the vessel there were two thin tubes connecting with the inlet and outlet parts on the head, and these tubes were curved so that the inlet stream impinged on the upper surface of the separator, while the liquid outlet

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4. Description of Sump Phase Operations (a)(cont'd.)

line naturally dipped down toward the bottom. On the upper head there was a gas outlet connection, and this head also carried an internal pipe to take gas out of the top of the chamber. The separator was equipped with a liquid level control to automatically regulate the fluid volume.

The non-condensable gases, still at high pressure, entered the suction ring of the recycle gas system. This suction ring connected the outlet sides of several coal stalls and helped to simplify the gas purification and recirculation system by equalizing the pressures and reducing the number of control instruments. The hydrogen content of the outlet gas had been reduced to about 60 percent, and it was necessary to partially purify it before using it again in the sump phase. An oil scrubbing system operating at the system pressure, was used to selectively remove part of the methane and higher hydrocarbons and thus maintain the purity of the recycle gas. The principal parts of the purification system consisted of absorption towers, solvent circulating pumps, and power recovery engines with necessary gas-liquid separators. The towers were steel forgings that varied in size from 1000 millimeters by 12 meters to 1300 millimeters by 15 meters long. They were usually packed with Raschig rings and adapted for gas inlet and liquid outlet connections at the base and gas outlet and solvent inlet at the top. The usual hourly through-puts were about 75 cubic meters of solvent to 50,000 cubic meters of gas for the larger size tower, although the liquid to gas ratio was adjusted to give an outlet hydrogen purity of 70-75 percent.

The solvent, containing dissolved hydrocarbons and hydrogen, was next expanded to about 50 atmospheres in expansion engines, and the power recovered was used to circulate part of the solvent within the process. The gas separated at this pressure was lean in higher hydrocarbons, and was used for cracking or fuel purposes. The liquid was then blown down to atmospheric pressure, and this gas, which contained an important propane-butane fraction, was treated to recover these materials as is described in Section 6. The regenerated solvent was then recirculated to the towers.

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4. Description of Sump Phase Operations (a)(cont'd.)

As previously explained, the gas outlet streams from several coal stalls were connected, and this header fed impure gas to a series of washers all operating in parallel; the number of units of course varied with the quantity of gas to be treated. The gas outlet streams from the washers were also connected into a manifold that served several booster compressors. These were single stage machines that handled between 50-80,000 cubic meters per hour at differential pressures from 50-80 atmospheres. The outlet gas from the circulating compressors was mixed with fresh paste and started another cycle through the apparatus.

The light liquid products in the intermediate separator and the cold separator were expanded stepwise in two or three stages to atmospheric pressure. When a two step system was used, the intermediate pressure was usually 50 atmospheres, and the flashed gas, being quite lean, was used for fuel. The gas from the atmospheric pressure expansion was treated to remove C_2-C_4 , as described in Section VI, while the liquid was distilled to yield a heads fraction of 325° E.P. called middle oil A, and a heavier residue oil that was recycled for pasting of coal. The middle oil A was treated in the gas phase, as described in Section V, to make gasoline and diesel oil, and this middle oil constituted the primary product from the sump phase. The distillation procedures and gas treatments are both covered in more complete detail in Section VI on Products Separation.

The heavy oil and solids that were left in the bottom of the hot separator were cooled by counter-current heat exchange with part of the fresh hydrogen make-up gas and finally by water to about 200° C. The slurry was then blown down to atmospheric pressure through special valves operated by the liquid level controller. These valves had replaceable stem faces and seats of tungsten carbide, to resist the abrasions of the solids. See drawing no. C-8 in appendix C for the details of construction of the expansion valve. A large expansion chamber was used after the seat to reduce the pressure drop across the valve and increase the life of the seat. In operation the valves were opened wide for a few moments and then shut, for if they had been used to

4. Description of Sump Phase Operations (a)(cont'd.).

throttle, the seats would have been cut out in one to two hours. By operating the valves in pairs, each one working singly for about 15 minutes, the average working life was about 500-600 hours. The replacing of the seats and stems was not difficult, for a valve could be reconditioned in about 15 minutes while the twin was operating.

The gas evolved from the sludge was usually used for fuel, and the slurry after dilution with oil was centrifuged to recover the pasting oil for the next cycle. The solids containing residue from the centrifuges was caked to recover additional pasting oil. These operations are covered more completely in Section VII, on Solids Removal and Oil Recovery.

(b) Processing of Bituminous Coals.

The bituminous coal fields in Germany were located in two principal areas, the Ruhr and Silesia; and in both of these districts the Germans had large coal hydrogenation plants for the production of motor fuels. Bituminous coals differed in composition from the previously discussed lignites, since they were much older geologically, and had lost a major portion of the oxygen as well as part of the hydrogen so that the hydrogen-carbon ratio was lower than that of lignite. The condensed ring structure of the coal gave the resultant oils higher aromatic and naphthenic contents than those from lignite. An average analysis of bituminous coal, on a dry basis was 5 percent ash, 78 percent carbon, 5 percent hydrogen, 1 percent nitrogen, 3 percent sulfur, and 8 percent oxygen. In general the Ruhr coals were a little older than the Silesian and had a slightly lower hydrogen to carbon ratio, but this difference did not seem to affect the coal through-put greatly.

The mechanical operation of the sump phase for bituminous coal hydrogenation differed in a few respects from that employed with lignites. However, since the same types and sizes of equipment were used, and since most of the major features were similar, only the points of difference will be described in this section. There were two systems

4. Description of Sump Phase Operations (b)(cont'd.)

of operation which varied chiefly in the manner in which the feed paste was heated. The first or older method, as practiced at Gelsenberg and Scholven used only one heat exchanger, but had two preheaters. Bituminous coal paste of the desired concentration could not be used in a heat exchanger, as was done with brown coal, on account of the swelling and fouling of the tubes, and hence it was necessary to heat the paste plus a small stream of gas in a gas-fired preheater section. The major portion of the hydrogen stream passed through the heat exchanger counter-current to the outlet products, as in the case of brown coal, and was then united with the hot paste. This mixture of gas and paste, was then heated in a second preheater section up to 425°C. before entering the converters.

This system was obviously less thermally efficient than the standard brown coal process, and this was aggravated by the extremely low heat transfer coefficient of about 6 kilo calories per square meter per hour per degree Centigrade which was obtained in the gas-fired preheater. Therefore, research was conducted to try to adapt the brown coal technique to bituminous coal. (16,17,18) It was found that coal pastes of about 35 percent concentration operated satisfactorily in the heat exchangers with heat transfer coefficients similar to those obtained with brown coal paste. (17) Therefore, a new method of operation was developed in which the total coal paste was made up into two batches. A thin coal paste of 36 percent fresh coal was preheated together with about 90 percent of the recycle hydrogen in a series of three heat exchangers. A thick coal paste containing about 48 percent coal was heated with 10 percent recycle hydrogen in a gas-fired preheater, and then the two streams were combined. The composite mixture was heated to 425°C. in a preheater in exactly the same manner as was done with brown coal. The ratio of thin paste to thick was usually about 1.1 to 1.2 and the combined paste contained about 41 percent coal. This second method of operation, as practiced at Politz and Oberschlesien, reduced the heat requirements by nearly 50 percent, and at the same time it greatly lowered the pressure drop through the unit.

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4. Description of Sump Phase Operations (b)(cont'd.)

The asphalt contents of bituminous coals were considerably higher than those of lignites, and since these materials were very refractory toward hydrogenation, it was necessary to operate the sump phase converters at 485°C. In most of the plants the operating pressure was 700 atmospheres, (19) since the higher hydrogen pressure had a very pronounced effect on the asphalt decomposition. The catalysts used were 1.5-5 percent of "Bayermasse" or "Roterz", 1.3 percent iron sulfate, and 0.3 percent sodium sulfide, all based on the weight of coal. These materials were mixed with the coal and ground in a mill in the same manner as was done with lignite.

Each coal stall usually contained four 1000 millimeter diameter by 18 meter long converters giving a total reaction volume of 36 cubic meters. The coal paste through-puts averaged between 33 and 37 tons per hour, which gave a contact time of very nearly one hour. The gas volumes were 30,000 cubic meters per hour circulated with the paste, and 20,000 for temperature control in the converters. The hydrogen consumption per ton of middle oil produced averaged about 1600 cubic meters, while the conversion factor for middle oil from coal was 0.6 tons per ton. The conversion of bituminous coal was quite high, about 95 percent of the carbon being transformed into gaseous and liquid products.

At Scholven the hydrogenation plant operated at 300 atmospheres pressure, since a more active catalyst was used. A mixture of tin oxalate and ammonium chloride, 0.06 and 1.0 percent, respectively, based on the weight of coal was added to the paste. This catalyst gave the less favorable conversion of 90 percent of the coal at through-puts comparable to those used in other plants. There were, however, mechanical difficulties in operation, since the chloride was quite corrosive. (20) The two points where the maximum corrosion occurred were in the preheater tubes, and in the coolers where water started to condense and gave an acid solution of chloride salts. On account of the corrosion difficulties, the tin-chlorine system was not popular in Germany, and Scholven was the only plant so operated.

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4. Description of Sump Phase Operations (b)(cont'd.)

Bituminous coal middle oils were richer in aromatics and naphthenic compounds than those obtained from brown coal, and the gasoline made from them had good octane ratings. The description of the further processing of these middle oils to produce fuels is described in Section V.

(c) Processing of Tars and Pitches.

The hydrogenation of coal tars and pitch played an extremely important part in the German fuel program for the war. There were at least six large plants which processed only tars and pitches from the numerous coke ovens, and in addition to these, nearly every coal hydrogenation plant used some tar mixed with the paste to increase its production. Low temperature tar from brown coal was the principle raw material, and this tar contained about 81 percent carbon, 11 percent hydrogen, 1.5 percent sulfur, 0.5 percent nitrogen, and 6.0 percent oxygen. The phenol content was about 10-15 percent.

The crude tar as received, contained about 2 percent water and 1 percent of fine dirt. These materials were separated in centrifuges, since it was necessary to remove the water to prevent crusting and overheating of the tar in the still preheater. The latter was caused by sudden vaporization of the water with subsequent stagnation and carbonizing of the tar. The dirt was removed to protect the sump phase catalyst from being fouled and its activity reduced. After removal of the dirt and water, the purified tar was distilled, giving a middle oil plus gasoline fraction boiling below 320°C, and a heavy residue. This latter material, which amounted to about 55 percent of the tar, was treated in the sump phase, to produce additional middle oil.

The catalyst most frequently employed for tar hydrogenation was iron sulfide on coke breeze such as that obtained from coke ovens or Winkler generators. About 0.5 - 1.0 percent of this powder was made into a paste of about 40 percent concentration using freshly stripped tar residue oil for a vehicle. This paste was mixed with about one hundred

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4. Description of Sump Phase Operations (c)(cont'd.)

times its volume of heavy slurry from the hot separator at the entrance to the heat exchangers and pumped with the fresh tar through the unit. The catalyst concentration therefore was about 4-5 percent of the tar feed.

The operation of the sump phase with tar was nearly the same as with brown coal, the chief difference being the greatly reduced solids removal problem. (See drawing no. 3) A small bleed, corresponding to approximately the quantity of fresh catalyst paste, was withdrawn from the hot separator and centrifuged to recover the oil. A hot recycle oil pump, located in the system, recirculated slurry from the hot separator back to the inlet of the preheater and thus increase the turbulence in the converters.

In general the hydrogenation of tars and pitches could be classified into two chief types of operation. The brown coal tars which were low in asphalt (2-5 percent) required less drastic condition than did the pitches and cracking residues which were high in asphalt. For materials in the first category a reaction temperature of about 450-460°C and a pressure of 300 atmospheres were employed. The through-put of fresh tar averaged about 0.5 tons per cubic meter of reaction volume per hour, and for each ton of tar, approximately 1000 cubic meters of gas were circulated. The heat of reaction was much less, averaging about 120 kilo calories per kilogram of middle oil produced, and hence the temperature control in the converters was much easier. Since coal tar had a higher hydrogen content and lower molecular weight than coal, greater yields of oil could be obtained than with coal. About 30 percent more middle oil was produced in a given unit (that used coal tar) and the hydrogen consumption was approximately 250 cubic meters per ton of middle oil, or about 15 percent of that required for coal. In general the brown coal tars were easily handled in the sump phase, and they were a desirable raw material for gasoline production.

The hydrogenation of high asphalt tars and cracking residues was conducted at Lutzkendorf, where a pressure of 700 atmospheres and a temperature of 500°C. was required to

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DRAWING No. 3

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

4. Description of Sump Phase Operations (c)(cont'd.)

give satisfactory conversion. On account of the refractory nature of the material being processed, the through-put was low. It averaged about 0.35 to 0.40 tons per cubic meter per hour. A very high hydrogen partial pressure (92 percent) was maintained in the gas in order to accelerate the asphalt decomposition, but outside of the more drastic conditions required, the rest of the operation was the same as with brown coal tar.

The hydrogenation of pitch, as typified by the operation at Welheim (See drawing no. 4) was conducted at 480°C and 700 atmospheres pressure. The feed consisted of 60 percent fresh pitch with a 70°C melting point plus 40 percent heavy recycle oil from the process. The feed rate averaged 25 cubic meters per hour of liquid, and 45,000 cubic meters of gas were used per stall of four converters having a total reaction volume of 36 cubic meters. The hydrogen consumption was considerably greater than in plants processing brown coal tar, since pitch was a material relatively poor in hydrogen. On the average, 700-800 cubic meters of hydrogen were required to convert one ton of pitch to middle oil and fuel oil. The overhead oil collected in the cold separator was distilled to give a middle oil fraction for processing in the gas phase, while the residue was sold for fuel oil. This last operation was quite different from that practised in plants treating coal tars, since there the distillation residue was recycled. The high asphalt content of the pitch, and its low susceptibility to hydrogenation made further treatment of the heavy oil less attractive than in the case of tar. With a market for fuel oil, this provided a convenient way of keeping the asphalt content in the system from becoming too great. The gasoline produced from pitch had a good octane rating on account of its high aromatic content. The preparation of gasoline from pitch middle oil is described in Section V.

5. Description of Gas Phase Operation.

As previously mentioned, the purpose of the gas phase was to take the liquified coal or middle oil from the sump