3.   General Outline of Hydrogenation.

The hydrogenation of coal was performed in two stages since it was impossible to treat coal directly with active catalysts without subsequent loss of catalyst activity due to fouling of the surface. Therefore, in order to produce high anti-knock gasoline the coal was first liquefied and the resultant low molecular weight, clean oil was destructively hydrogenated over active catalysts to produce a gasoline of good octane number.

The first stage of the process was commonly called the sump or liquid phase (see drawing No. 1). After the coal had been dried and crushed it was mixed with heavy recycle oil from the process and ground into a paste. Usually about two parts of coal were mixed with three parts of recycle oil plus small amounts of catalyst. The resultant viscous paste was raised to the operating pressure of either 300 or 700 atmospheres in large, hydraulically-operated paste pumps. Most of the plants operated the sump phase at about 700 atmospheres since both the through-put of coal and the decomposition of asphalt were higher. The paste was next mixed with recycle hydrogen and passed through heat exchangers counter-current to the outlet products from the process. The heat exchangers supplied between 50 and 90 percent (depending upon the plant) of the heat required to bring the paste-gas mixture up to temperature. The additional heat was supplied in a tubular, gas-fired preheater.

The paste left the preheater at a temperature of about 425°C and entered the bottom of a series of three or four large, unpacked converters. These converters were large steel forgings about one meter inside diameter by 18 meters long, internally insulated to maintain a relatively cool pressure shell. The hydrogenation of coal was a highly exothermic reaction, and hence sufficient heat was liberated to raise the feed to the reaction temperature of about 470-485°C in the first few meters of travel in the first converter. The temperature was controlled by injecting cold hydrogen at three or four different points in each converter. During the passage of the paste-gas mixture through the reactors, about 95 percent of the carbon in the coal was

DRAWING No. 1

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

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

converted to gaseous and liquid products, and these latter were destructively hydrogenated to lower molecular weight products. Thus the material leaving the last converter after a contact time of about one hour at approximately 475°C had a viscosity near that of water.

The oil and gas next entered a hot separator which was a large steel vessel internally insulated, where the gaseous products and the liquid plus solids were separated. In the process of separating the two phases, a large proportion of the more volatile oil constituents were stripped out and carried along in the gas stream. The hot separator, therefore, produced a crude separation of the products of the sump phase and simplified the handling of the light oil. The oil and gas vapors, after leaving the separator, were partially cooled by counter-current heat exchange with the incoming paste and gas and then given a final cooling in a water cooler. The condensed liquid was collected in a cold separator, while the gas was purified in a oil scrubber and recycled in the process. The condensed oil was expanded stepwise in either two or three stages to atmospheric pressure. The gas evolved from the first expansion was lean in higher hydrocarbons, and it was usually used for fuel. The gases from the other stages were treated to recover the C3 and C4 fractions which could be used as alkylate or bottled gas for vehicles. The oil was distilled and produced a light heads product with an end point of about 325°C called middle oil A. The residue oil was recycled for pasting of fresh coal.

The heavy slurry in the hot separator contained the solids left from the hydrogenation reaction. These solids were largely catalyst, ash, and unconverted coal, and amounted to about 20-25 percent weight of the slurry. This material was cooled to about 200°C and then expanded to atmospheric pressure through special valves that had hard alloy stems and seats to resist abrasion from the solids. The viscosity of the slurry was cut by the addition of about 25 percent of a light oil, such as middle oil A, and the diluted mixture fed to continuous centrifuges. These machines were conventional high gravity, automatic solid ejection-

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

type centrifuges, and they produced a clarified oil containing about 5-10 percent of finely divided solids and a residue that had a solid content of 35-40 percent, The oil was recycled for pasting purposes while the thick residue was coked in a steam distillation unit to recover about 75 percent of the oil. This latter oil was also used for pasting, while the dry residue was either discarded or mixed with coal and burned.

The middle oil A which was the chief product of the sump phase, contained too much oxygen, nitrogen and sulfur compounds to be used directly for gasoline. Hence, it was necessary to reduce these compounds and add more hydrogen in order to make satisfactory fuels. This part of the process was called the gas phase and was usually conducted in two stages when aviation gasoline was desired. The oxygen and nitrogen compounds existed in the sump phase oil mostly as phenols and nitrogen bases, respectively. As they were poisons for the active catalyst employed in the gasoline production stage, it was necessary to remove them. This was accomplished in a catalytic process called the prehydrogenation stage. This operation was conducted at 300 atmospheres and 400°C over pelleted tungsten sulfide (catalyst 5058) in a plant that was much like the sump phase. These converters, however, were equipped with trays to hold the catalyst. Between each two catalyst beds was a system of baffles which served to mix the hot oil and gas vapors with cold hydrogen introduced to control the temperature. Usually three or four converters connected in series were used in this stage and a contact time of about 1-1/3 hours was sufficient to hydrogenate the aromatics to naphthenes and to reduce the oxygen, nitrogen, and sulfur compounds to hydrocarbons with the formation of water, ammonia, and hydrogen sulfide, respectively.

The temperature was purposely held low in this stage to avoid excessive cracking, since the function of the prehydrogenation step was only to saturate the oil with hydrogen and to destroy compounds which would poison the gasoline production catalyst. The products of the 5058 stage were distilled giving a small gasoline cut which could

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

either be blended with alkylate or processed in the next stage. If desired, diesel oil could be removed as a fraction boiling over 200°C. Usually, however, most of the diesel oil was left in the middle oil B fraction boiling over 150°C and was processed in the next stage to make aviation gasoline.

The middle oil B, which consisted mostly of naphthenes and normal paraffins, was treated in the gasoline production stage over a catalyst consisting of tungsten sulfide and activated clay (catalyst 6434). The equipment for the process was similar to that used in the 5058 stage, but the temperature was a little higher, about 425°C. The oil throughput was a little greater so that the contact time averaged about one hour. The function of the 6434 catalyst was to crack open the naphthenic rings and to isomerize normal paraffins to iso-paraffins. At the same time a reduction in the average molecular weight of the oil occurred so that a huge fraction of the oil boiling over 200°C was converted into gasoline. The liquid product from the gasoline stage was distilled to give aviation gasoline that had an unleaded octane number of 70 to 75. The addition of 0.12 vol% of lead tetaethyl increased this value to between 90 and 95. The heavier oil left after the removal of the gasoline fraction was recycled together with fresh middle oil B to the 6434 stage.

As mentioned in the introduction, a considerable fraction of the German gasoline supply was produced by the hydrogenation of tar and pitch. These materials were easier to handle because they were already in a liquid state, and hence the mechanical problems attendent on the solids removal were much simplified. Furthermore, the hydrogen contents were greater in these materials than in coal, thus both the hydrogen consumption and the operating difficulties caused by coking were greatly reduced.

Tars and pitch were handled in a two step process in much the same manner as the coal. The crude tar was given an initial distillation to remove the gasoline and middle oil. The latter treated either directly over 6434 catalyst,

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

if the phenol and nitrogen contents were low or given a pre-hydrogenation treatment as was done with sump phase oil from coal if they were too high. The heavy distillation residue was processed in the sump phase under conditions very simi-lar to those employed with coal, although the through-puts were a little greater. The treatment of the sump phase middle oil was usually carried out directly over 6434 cata-lyst, as the phenol and nitrogen contents of the oil were low. The yields and quality of the gasoline so produced were inferior to that produced where a prehydrogenation stage was used, but a considerable saving in investment was realized by the elimination of one high pressure operation.

A new process to produce lubricating oils by hydrogena-tion was developed in 1936 by the I.G. Farbenindustrie and first put into plant operation at Zeitz in 1939. The low temperature hydrogenation process (known as T.T.H.) treated brown coal tar over an active catalyst such as 5058 in the sump phase at $390-410^\circ C$ and 300 atmospheres pressure. Very little cracking occurred, but instead a refining of the oil took place through the elimination of oxygen, nitrogen, and sulfur. Brown coal tar has a high paraffin content, and the purpose of the T.T.H. process was to preserve the paraffins, while hydrogenating the aromatics to naphthenes. Therefore, if the temperature was allowed to rise, the yields of lube oils and paraffin wax decreased, and greater quantities of diesel oil and gasoline were produced. The diesel oil manu-factured by the process had a cetane number of about 50 and the lube oils had a V.I. of 60-80.

Another new process which attracted quite a lot of at-tention in the literature, but which actually played a very minor part in the German fuel program, was the Pott-Broche process for the extraction of bituminous coal. Only one unit had been built and the output from this unit was large-ly coked to make electrode carbon. In practice the bitu-minous coal was extracted at about 100-150 atmospheres pres-sure and $420^\circ C$ in the liquid phase using a tetralin-cresol mixture. The product was filtered to remove solids, the solvent distilled off and recycled, and the asphalt-type residue processed in the sump phase like pitch. The opinion

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 in-
sulation, than for fuels.

The various steps of the coal hydrogenation processes
are discussed in greater detail in sections 4 to 9 enclusive,
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 occured 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, grind-
ing, 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 con-
sequently, 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 re-
cycle oil from the centrifuges with dried coal in ball or
mixing mills and wet grinding until the coal had been pro-
perly 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-

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