

## 5. Description of Gas Phase Operation (b)(cont'd.)

sure was 700 atmospheres. The equipment and method of operation, outside of the details mentioned, were quite standard. This catalyst was not nearly as active as the tungsten-containing ones, and hence the higher temperature was required to produce a suitable reaction velocity. At 500° C., however, the equilibrium was unfavorable for complete hydrogenation, so that the resulting gasoline was rich in aromatics. Thus a product was produced that had an octane rating of about 80 which could be raised to 92 by the addition of lead.

More complete details, including tables of analyses, on the various products produced in the gas phase may be found in Section X.

## 6. Hydrogenation Products Separation.

### (a) Gaseous Products.

The principal constituents in the gases from the various phases of the hydrogenation process consisted of saturated hydrocarbons methane to butane and higher, carbon dioxide, carbon monoxide, ammonia, and hydrogen sulfide together with hydrogen and a little nitrogen. In general the gases were divided into two groups, called lean and rich depending upon the relative amounts of propane and heavier which they contained and the degree of saturation. The amounts of heavier hydrocarbons carried by the gases depended upon the temperature and pressure of the mixtures, or more simply on the ratio of the partial pressure of each constituent to the total pressure. Gases from the intermediate expansion stages (50 atm.) of the cold and intermediate separator oils and circulating gas stream scrubber liquid were usually used for fuel directly. Since they contained chiefly hydrogen and methane, there were insufficient heavier hydrocarbons to warrant the expense of treatment.

The gases from the atmospheric pressure gas-liquid separators in the light oil and solvent systems previously mentioned were combined into a rich gas fraction. When an

6. Hydrogenation Products Separation (a)(cont'd.)

intermediate expansion of liquid from 50 atmospheres to about 5 atmospheres was used ahead of the final atmospheric pressure break down, the gas from this 6 atm. stage was also combined with the rich gas fraction. These gases contained the major portion of the propane and butanes produced during the sump and gas phase operations, and were treated to recover these materials.

The first step usually was an Alkacid treatment to remove hydrogen sulfide and carbon dioxide from the gases. The Alkacid process consisted in "scrubbing" the gases with an alkaline solution of either alanine or glycol derivatives in a system that operated in approximately the same manner as the conventional triethanolamine process. Further details on this step may be found in the gas purification section of U. S. Naval Technical Mission in Europe Report entitled "Production of Hydrogen and Synthesis Gas from Solid and Gaseous Fuels". (9)

The gases were next treated in a combination absorption distillation column at 15 atmospheres to remove the gasoline fraction which consisted of pentanes and heavier hydrocarbons. The lighter hydrocarbons and hydrogen were then given a water wash under pressure to remove ammonia before they passed to the butane column. In this unit butane and the small amount of pentane in the gas were removed from the base of the column while the lighter materials passed on to the propane column. Here the gases were separated into fuel gas and propane fractions. If desired the ethane could be separated from the fuel gas, but in most plants this was not done.

All of these hydrocarbon gas separations were performed in conventional equipment and according to standard practice, hence, there is no necessity to go into further detail concerning the technique of operation. The propane-butane fraction was either processed into high octane aviation gasoline by alkylation or polymerization or compressed, liquefied, and sold as motor fuel (Treibstoff). The output of this latter fuel usually amounted to about 10 percent of the gasoline production and hence represented

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6. Hydrogenation Products Separation (a) (cont'd.)

a sizeable contribution to the German fuel program.

(b) Liquid Products.

The liquid products described in this section were those obtained from the cold and intermediate separators in the sump phase and the cold separator in the gas phase. The treatment of the heavy oil slurry from the hot separator is discussed in Section VII. The liquid products from the cold separator were expanded to atmospheric pressure and the gas removed for separate treatment as has been previously described. The oil and water phases were then separated by decantation. The water, containing phenols, hydrogen sulfide, carbon dioxide, and ammonia, was usually treated with either tricresyl phosphate or phenolsolvan solution to remove the phenols in the same manner as aqueous liquors from cooking plants. Then the water was given an Alkazid treatment to remove the hydrogen sulfide before discharging to avoid pollution of the river. Further details on the treatment of water prior to discharge from hydrogenation plants may be obtained in U. S. Naval Technical Mission in Europe Report No. 87-45. (15)

The oil phase from the sump stage cold separator was sent to the "A" distillation unit. See drawing no. 7 for a diagrammatic flow sheet of the distillation process. Here the crude oil was partially preheated by counter-current heat exchange with the vapors from the still and then the hot still residue before it was further heated in a gas-fired preheater. This unit was similar in principle to the preheaters used in the gas and sump phases of the hydrogenation process. About 10 percent of steam was injected with the oil during the preheating in order to reduce cracking of the oil and carbon deposition on the tubes. The hot feed then entered a packed distillation column where it was separated into middle oil "A" and residue fraction.

The fractionating column was about two meters in diameter by 30 meters high and packed with Raschig rings. With a reflux ratio of 2 to 1 the average through-put was 65 tons per hour, the maximum 80 tons per hour. The end point of

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DRAWING No. 7

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

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## 6. Hydrogenation Products Separation (b)(cont'd.)

the heads product was usually held at about 320°C, and the separation was such that there was an overlap of about 10°C between the end point of the middle oil and the initial of the residue. The vapors were condensed in a series of three units, the first using the crude feed as the cooling medium, and the latter two using water. The gases were sent to the rich gas separation unit and treated as previously described, while the middle oil was separated from the water. The latter contained sufficient phenols so that it was treated to recover these materials in the same manner as the aqueous phase from the hydrogenation units.

The whole distillation process was quite conventional and simple. The fractionation was not very sharp, since the principle object was to produce a light oil for the gas phase process, that was free of high molecular weight tarry materials. The condensed oil collected in the first or oil cooled condenser was usually blended with the rest of the oil, but part of it could be kept out for pasting purposes if desired. The residue was used for pasting in the sump phase.

The distillation of the gas phase cold separator product was conducted in essentially the same type of apparatus, but there were more variations depending upon the desired products. When brown coal or brown coal tar was hydrogenated the product of the 5058 prehydrogenation stage was often fractionated into a gasoline of 140-150°C E.P. which was then processed in the DHD unit to make aviation gasoline and a residue of middle oil B for treatment in the 6434 stage. Sometimes a portion of the middle oil was taken out as diesel fuel, a cut from 200°C to 300°C usually being removed for this purpose. When bituminous coal was processed, it was customary to pass the whole product of the 5058 stage to the 6434 stage unless a DHD gasoline stock was removed.

The oil product from the 6434 phase was also distilled in similar equipment to produce aviation gasoline of 150-165°C end point and middle oil which was recycled to the same hydrogenation stage. The gasoline was stabilized and the lighter materials sent to the rich gas treatment unit.

6. Hydrogenation Products Separation (b)(cont'd.)

All of these distillation stages were quite conventional in operation, and hence this phase of the coal hydrogenation process is not discussed in detail. Some of the important properties of the various motor fuels and gasolines are presented in tables in Section X of this report, but for more detailed information about aviation gasoline the reader is referred to U. S. Naval Technical Mission in Europe Report entitled "The Manufacture of Aviation Gasoline in Germany" (24) U. S. Naval Technical Mission in Europe Report entitled "German Diesel Fuels" gives more complete information on the characteristics of diesel oils produced by hydrogenation.

7. Sump Phase Solids Removal and Oil Recovery.

(a) Centrifugation of Slurry.

In the hydrogenation of the coal a small fraction was not converted during the passage through the converters, and this together with the coal ash and catalyst had to be removed from the cycle. The most common way was to centrifuge the slurry from the hot separator into a clarified recycle product plus a heavy sludge that contained most of the solids.

The hot slurry from the hot separator, after having been cooled to about 200°C and blown down to atmospheric pressure, as described in Section IV, was diluted with a lighter oil to reduce the viscosity. The solids content in the original slurry was usually about 20-22 percent, and approximately 25 percent of diluent oil was added, so that the resultant solids content was about 16 percent. The choice of thinning oil played an important part in the operation of the sump phase, since the characteristics of the pasting oil could be controlled at this point. The composition of the oil could be a blend of clarified oil from the centrifuging, the residue from the cold separator distillation after removing the middle oil, and middle oil itself. The use of the clarified centrifuge oil helped to reduce the asphalt content in the system, since on a second pass through the machine an additional quantity was removed with the solid residue. The use of some middle oil in the diluting feed helped to thin the slurry more, and at the same time it pre-