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 per-
cent) was maintained in the gas in order too accellerate
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 opera-
tion at Welheim (See drawing no. 4) was conducted at 480°C
and 700 atmospheres pressure. The feed consisted of 60 per-
cent 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 consump-
tion 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 hy-
drogen 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 pro-
vided 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

DRAWING No. 4

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

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

phase and, by a combination of hydrogenation and cracking, convert it into gasoline. At first this operation was conducted in one step over a molybdenum-magnesium-zinc catalyst (No. 3510) at temperatures around 460°C. This catalyst, however, produced too much gas and its activity was rather low, so that the through-put of oil was small. In 1933, after laboratory tests at Ludwigshaven, the I.G. plant at Leuna first tried pelleted tungsten disulfide catalyst (No. 5058) in the place of 3510.(21) This new material was about three times as active as the first catalyst, and hence it was possible to operate at a lower temperature and obtain a superior product with better yields. The tungsten sulfide was very active in hydrogenating aromatics to naphthenes as well as reducing phenols, nitrogen bases, and sulfur compounds to hydrocarbons. However, the high proportion of naphthenes and paraffins in the gasoline produced by this method gave a low octane number of about 60. By the addition of lead this could be made into motor gasoline, but not aviation grade. The diesel oil on the other hand was of fair quality, the cetane number falling between 35 and 50.

Since the German emphasis was upon aviation grade gasoline, a search was made for a catalyst that could convert naphthenes and normal paraffins into isoparaffins. In 1937, Leuna started to use a tungsten sulfide-activated clay catalyst (No. 6434) to convert the product from the 5058 stage into aviation gasoline. The unleaded gasoline produced by this material had an octane number of 70 to 75, which by the addition of tetraethyl lead, could be easily raised to aviation grade. This latter catalyst could not treat middle oil from the coal sump phase directly, since the phenols and nitrogenous bases in the oil poisoned and drastically reduced its activity. Therefore, it was necessary to pretreat the sump phase oil with 5058 catalyst to remove the oxygen and nitrogen compounds before using the 6434 catalyst. This resulted in a two stage gas phase operation which continued with only minor changes throughout the war. However, when only auto gasoline or diesel oil were required, a one step process using 5058 catalyst was employed. Obviously, many variations of these processes could be used, depending

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

upon the particular demands, but the use of 6434 to make
aviation gasoline, and of 5058 to make diesel oil and motor
gasoline became the basis of the German synthetic fuel pro-
gram for coal hydrogenation.

   (a) Prehydrogenation Stage.

   The feed for the prehydrogenation was usually middle
oil from the sump phase hydrogenation of brown or bitum-
inous coals and tars. To this was added a recycle middle
oil from the distillation of the product. A typical analy-
sis of a bituminous coal middle oil was: specific gravity
0.956 at 20° C.; aniline point -12.5° C.; phenol content
17%; and distillation range 145-322° C.

   The oil was pumped up to the operating pressure of 300
atmospheres in large pumps quite similar to those used for
handling coal paste. The maintenance on these oil pumps
was less, however, on account of the absence of solids and
the consequent reduction in abrasion of the pistons and
packings. Hydrogen was next added to the oil from the pres-
sure header which contained recycle plus make-up hydrogen.[9]
About 1500 cubic meters of gas containing between 70 and 80
percent hydrogen were circulated for each cubic meter of
oil feed.

   Referring to drawing no. 5, which shows a typical flow
for the gas phase, it will be seen that the oil and gas
mixture entered the bottom of the first of two heat exchang-
ers. These pieces of equipment were built exactly like the
ones used for the sump phase, and operated in the same man-
ner with the inlet material on the outside of the tubes
flowing upwards and the outlet products on the tube side
flowing down. The sizes varied with the plant, but two of
the most common were the 500 millimeter diameter with 151
tubes, and the 600 millimeter diameter with 199 tubes.
These two exchangers were both 18 meters long and had heat
transfer surfaces of approximately 145 and 190 square meters,
respectively. A new design of the 600 millimeter heat ex-
changer had been made in which there were 241 tubes having
a total surface area of 228 square meters. This later ap-

DRAWING No. 5

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attached at the end of this report)

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

paratus had probably been planned for new gas phase installations since its use was not in evidence in the plants visited.

With a feed rate of approximately 20 cubic meters of oil plus 20,000 cubic meters of gas per hour entering the cold heat exchanger at near room temperature, the heat transfer warmed the feed to about 180° C. In the second or hot exchanger the feed was further heated to about 300° C. The overall heat transfer coefficients were usually about 250-300 kilo calories per hour square meter degree centigrade (51-61 BTU per hour per square foot degree Fahrenheit), although at times under favorable circumstances the values went as high as 400-500 metric units.

As in the sump phase, it was necessary to give the feed a little additional heating in order to warm it to the point where the heat of reaction was sufficient to carry the temperature up to the reaction zone. In the sump phase, gas-fired tubular preheaters were used exclusively. In the gas phase, gas-fired preheaters similar to those employed in the sump phase were used in some installations, while in others electrical heat was used. The former type has been described in section IV, but the latter equipment was employed only in the gas phase operation.

The preheater consisted of four to six 120 by 90 millimeter tubes of N8 steel, approximately 15 meters long, encased in a thin steel cylindrical shell. (See drawing no. C-9 in Appendix C). Instead of using heating elements, the tubes themselves were the electrical resistors, thus increasing the thermal efficiency. Steel lugs were welded on the outside of the tubes, and electrical connections were made to them through bus bars backed up with steel plates. The tubes were supported by ring clamps insulated from each other and from the steel shell at the top end. Rock wool insulation was packed around the tubes inside of the shell to reduce the heat losses. The transformers used to reduce the electric current operated on a primary voltage of 6000-7000 volts, and usually one was required for each pair of hair pin bends or four straight lengths. The hot side of

the secondary winding of the transformer was connected to the binding post connecting the tops of the two inside lengths of tubing, while the negative or grounded side of the transformer was connected to binding posts at the top of each outside length. Thus the electrical current flowed through one complete "U" bend, heating up the tube by reason of the I^2R loss in the steel. For obvious reasons, a low potential of about 70 volts and a high ampere current were employed in this type of apparatus. In general the electrical type of heater was satisfactory when its limitations were not exceeded.

One of the big advantages of the electrical type of preheater was that the heat input could be quite accurately measured, and thus better control could be obtained. The electrical type was also somewhat less expensive to build, and where the power load was not too high, the operating costs were reasonably favorable. However, there were several rather serious disadvantages connected with the electrical preheater. If the material being heated inside the tube started to carbonize, polymerize, or cake on the walls in any way such that the heat transfer was reduced, then the wall temperature of the tube increased, since the electrical input remained constant. The higher wall temperature increased the local electrical resistance, so that the greatest amount of heat was being liberated in the section where the heat transfer was the lowest, and this still further raised the local pipe temperature. If the contents in the tube continued to cake or coat, as was usually the case when the local temperatures became excessive, then the preheater tube would become heated to such a point that it would rupture and possibly cause a serious fire. For this reason, the electrical preheater could be used only on clean materials such as distilled oils, but even then gas-fired preheaters were often used.

Another liability, although not as great as the first, was caused by the increase in electrical resistance of the steel with temperature. Thus the greatest heat density in the tube was at the outlet end, whereas the reverse situation would have been more desirable on account of carbonization. This defect was partially overcome by heating the total length in short sections, as has been previously des-

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

cribed.

The oil and gas after having been heated up to approximately 350° C. in the preheater entered the first of a series of either three or four converters. The early converters were packed solid with catalyst, but the highly exothermic heat of reaction caused local overheating and made the temperature difficult to control. The next step was to introduce cold hydrogen at several points in the reaction zone by the use of internal down pipes of appropriate lengths. This method worked moderately well for the less active catalysts, but the mixing of the hydrogen and the reation products was not as good as desired. The more recent designs, therefore, supported the catalyst on several grates with a space between the top of one catalyst bed and the grate of the next one above. Cold gas was introduced to each section and mixed with the oil and hot gas vapors by means of baffles in the unpacked section, and better control of the temperature was obtained.

The new converters used for the gas phase hydrogenation (See drawing nos. C-10 and C-11 in Appendix C) were forgings of S2 steel, 1000 millimeters internal diameter by 18 meters long, and were fitted with an internal lining of diatomite insulation 65 millimeters thick, similar to that used in the sump phase converters. A thin stainless steel liner was used inside of the insulation to contain the reaction materials and resist the corrosive attack of high temperature hydrogen and hydrogen sulfide. The catalyst was held on grates, usually seven in number, although some designs used as few as four. These grates consisted of a series of steel strips set on edge with parallel spacing of about 10 millimeters. The ends were welded to the internal circumference of a steel hoop. Fastened to the lower side of the grating were two sets of baffles with slots set 90° to each other. Under the baffles was a perforated distributing plate. The previously mentioned cold gas lines were brought in through the top head and carried down in the insulation lining to points between the catalyst grates and the baffles. One line was used for each catalyst bed except the bottom, and the cooling gas was introduced through the stainless

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

steel liner into the space between the baffles and the grate.
The thermocouple well was located in the center of the con-
verter and temperature measurements were taken at the en-
trance and in the middle of each catalyst bed. The materials
of construction of the internal parts were of stainless
steel when available, but galvanized N5 steel was used when
the former was unobtainable.

The early catalytic converters employed an upward flow
of oil and gas, but it was found that the dust formation
was too great, especially with the lighter catalysts, due to
agitation of the particles by the ascending gas stream.
Therefore, the newer practice employed downward flow. Be-
tween 7.2 and 7.6 cubic meters of catalyst could be changed
to a converter, the difference depending upon whether seven
or four beds were used. The 800 millimeter converter was
constructed like the one just described, but of course the
catalyst volume was less, amounting to about 5 cubic meters.

The standard prehydrogenation catalyst consisted of
cylindrical pellets 10 millimeters in diameter by 10 milli-
meters high of tungsten disulfide. This material was pre-
pared by dissolving tungsten trioxide in ammonium sulfide
solution, and heating the resultant ammonium thiotungstate
in a stream of hydrogen to give tungsten disulfide. This
material was pelleted and used for the prehydrogenation
stage.[21] For more complete details on the preparation of
5058 catalyst see Appendix B. During the war tungsten be-
came quite scarce in Germany, and hence research work was
conducted to find a substitute catalyst which could replace
5058.[22] One of the better new materials was prepared from
activated alumina plus 25 percent of tungsten sulfide and
3 percent of nickel sulfide.[23] This composition, called
7846W250, was more active than 5058 in hydrogenating the
lower boiling constituents in the oil, but less active in
the reduction of phenols, and it was much weaker as a crack-
ing catalyst. The usual practice was to use a combination
of 5058 and 7846W250 in order to take advantage of the good
characteristics of each.

The standard method of operation was to fill all con-

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

verters with 5058 catalyst and use a pressure of 300 atmospheres and a temperature of 390-410° C. However, good operation was obtained when the first one or two converters were charged with tungsten disulfide and the others with 7846W250. The advantage of using the 5058 first was that it partially reduced the phenol content of the oil and made the temperature easier to control, whereas if the diluted catalyst had been used first, about 90% of the phenols would have been reduced in the first converter and the exothermic heat of reaction would have been difficult to dissipate.

When the prehydrogenation stage was properly operated at a temperature not over 410° C. the gas production was quite low, and the concentration of C_3 and C_4 hydrocarbons was very high. About 10 percent of the carbon would be converted to gaseous products of which about 50 percent would be C_4, 20-30 percent C_3, and the rest C_2 and C_1. The C_4 cut contained about 40 percent isobutane which was useful for alkylation. The liquid product from the prehydrogenation stage contained about 10 percent aromatics, 40 percent naphthenes, and 50 percent paraffins. The normal catalyst life was at least one year, but under favorable conditions it might last two years.

The mechanical operation of the gas phase was very similar to that of the sump phase. The through-put of oil averaged about 0.6-0.8 kilograms per liter of catalyst per hour, and the ratio of gas added as recycle was about 1500 cubic meters of gas per cubic meter of oil. An average hourly through-put, therefore, for a gas stall having four converters of 28 cubic meters catalyst volume, would be 20 tons of oil plus 30-35,000 cubic meters of recycle gas having a hydrogen content of 80-85 percent. Approximately 20,000 cubic meters of cooling gas would be divided between the four converters for temperature control. Each of the catalyst beds had its individual cooling gas line, and by regulating the amount of gas introduced into the baffled vapor mixing chamber below each bed, it was possible to keep the temperature under control. As previously mentioned, the usual flow was from top to bottom to prevent dust formation due to attrition of the pellets. The heat of reaction

5. **Description of Gas Phase Operation (a)(cont'd.)**

in the prehydrogenation stage was highly exothermic on account of the large amount of hydrogen added in saturating the products. The hydrogen consumption was about 500 cubic meters per ton of middle oil, and the heat of reaction was about 100-150 kilo calories per kilogram of middle oil.

About one cubic meter of water was injected into the hydrogenated middle oil and gas vapors after leaving the last converter to prevent salt formation, and the products were then cooled by countercurrent heat exchange with the inlet material. This was followed by a final cooling with water in a set of four to six parallel trombone coolers. The condensed oil was separated in a cold catch pot, and the gas recirculated without any purification. Where the same gas compression system was used for both the prehydrogenation and gasoline production stages, a water scrubber was used to remove the ammonia from the gas, but where each gas system was separate, it was not necessary to use the scrubber. Usually the outlet and inlet gas lines from several stalls operating on the same material were connected to a manifold, and a booster compresser was used to make-up the pressure drop in the cycle.

The liquid product from this stage, after reducing the pressure, was distilled (as described in Section VI) into gasoline which had an E.P. of 165° C. and the low octane number of 60. This gasoline could be improved by the addition of tetraethyl lead to make a satisfactory motor gasoline. The more modern treatment, however, was to take the prehydrogenation gasoline and treat it in a D.H.D. plant[24] in order to dehydrogenate naphthenes to aromatics and isomerize some of the normal paraffins to isoparaffins. By this treatment the octane number of 5058 gasoline could be raised to about 80.

The fraction of the prehydrogenation product boiling higher than gasoline was called middle oil B. This material was high in naphthenes and paraffins and hence a satisfactory diesel oil could be made from it. When the latter was desired, a side stream boiling from 200 to 300° C., was withdrawn from the still and sold. This diesel fuel had a cetane number of about 35 to 50.

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

(b) Gasoline Production Stage.

In the earlier days of coal hydrogenation the internal combustion engines did not require as high quality fuels as were needed during the war. It was possible therefore, to use the gasoline made by the tungsten disulfide catalyst directly after the addition of lead. Later, however, when a aviation gasoline of 87 to 100 octane was required, it was necessary to use another stage to convert the middle oil B into aviation gasoline.

The mechanical equipment and method of operation of this second or gasoline production step were identical with those used in the prehydrogenation stage, and hence will require very little explanation. The catalyst for this process (no. 6434) consisted of 10 percent tungsten sulfide plus 90 percent activated clay made into cylindrical pellets 10 by 10 millimeters. Fullers earth was activated with a hydrogen fluoride solution and a solution of ammonium thiotungstate in ammonium polysulfide added. After evaporating to dryness the product was heated in a hydrogen atmosphere to give tungsten sulfide and clay. The mixture was then pelleted and ready for use. For more complete details of the method of preparation, see Appendix B.

The middle oil from the prehydrogenation stage was mixed with recycle middle oil from the gasoline stage and processed at about 400-420° C. and 300 atmospheres pressure. The oil throughput was about 1.2 kilograms per liter of catalyst per hour, or 30 to 35 tons per hour in a four converter stall. The gas requirements were decidedly less, since the hydrogen consumption was about 200 cubic meters per ton of feed. The total gas recycled with the feed averaged about 20,000 cubic meters, while only 6 to 7,000 cubic meters of hydrogen were required to control the temperatures in the converters.

The sulfide catalysts required a partial pressure of hydrogen sulfide in the gaseous products in order to prevent reduction of the tungsten sulfide to inactive metal. The sump phase middle oil usually contained enough sulfur com-

5. <u>Description of Gas Phase Operation (b)(cont'd.)</u>

pounds, which upon hydrogenation supplied sufficent hydrogen sulfide to maintain the activity of the 5058 catalyst. The feed for the gasoline stage, however, was nearly sulfur free, and it was necessary to add hydrogen sulfide to the reactor. Hydrogen sulfide could be added in any of several ways, such as mixing with the feed gas, pumping liquefied hydrogen sulfide, or by using a hydrogen-hydrogen sulfide gas mixture for cooling in the converters. The latter method was quite popular, since it reduced the corrosion in the heat exchangers and preheater. The optimum sulfur content was about 2 percent, but in practice it was usually between 0.5 and 1.0 percent, since the last 1 percent only added slightly to the activity.

This catalyst was very active in opening naphthenic rings, in reducing the molecular weight of the oil, and in converting normal paraffins to isoparaffins. Despite the cracking that occured, only a small amount of gas was formed. Approximately 8 percent of the carbon in the oil was converted to gaseous products which analyzed about 70 percent C_4, 20 percent C_3, and 10 percent C_1 and C_2. The C_4 cut furthermore contained approximately 75 percent isobutane. The C_5 fraction of the gasoline contained 80 percent iso and 20 percent normal pentane. All of these results were achieved only when the catalyst was properly operated. If the catalyst was accidentally poisoned and the temperature was raised, then the yield of methane increased, and the ratios of iso to normal paraffins dropped sharply. The normal life of 6434 catalyst was about one year, but much depended upon the type of feed. Unless the phenol, nitrogen, and high molecular weight compounds were kept to a minimum, the loss of activity was rapid. The first two types of compounds caused a temporary loss of activity, whereas the latter formed condensation products that could not be desorbed, and thus caused permanent impairment.

The liquid product was distilled to produce aviation gasoline and middle oil B for recycle. The gasoline had an E.P. of 150° C. and an octane number of 70 to 75. (Later in the war the E.P. was raised to 175° C. to increase production.) The lower octane value was obtained from brown

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

coal and brown coal tars on account of the high paraffin base, whereas the condensed ring structure of bituminous coal gave a naphthenic type of gasoline with a higher rating. By the addition of 0.12 volume percent of lead tetraethyl, the octane ratings were raised to between 89 and 92.

Several variations of the gasoline production stage were used. Among the more important were the use of 5053 catalyst to make gasoline, and the treatment of brown coal tar middle oil without prehydrogenation. In the former case the temperature was usually raised to about 420-430° C., and the residue middle oil recycled so that the end product was gasoline that could be converted into aviation fuel by DHD or leaded to motor grade. Since the DHD process could produce gasoline with an antiknock rating of 78 to 80, the single high pressure step for gasoline production was being more extensively used.(24)

Since coal tars did not contain a very high percentage of phenols or nitrogenous bases, several plants treated the mixture of middle oil from the distillation of the raw tar and sump phase product directly over the 6434 catalyst, thus producing gasoline in one gas phase step. The through-put was lower and, as must be expected, the catalyst life was shortened, but a saving in investment cost was realized. The octane rating of the gas was slightly poorer, the value being 69, but this could be made into an acceptable aviation fluid by raising the octane to 89 with the addition of lead.

The Ruhröl AG had a quite different method of producing gasoline from middle oil obtained from the sump phase hydrogenation of pitch. They had developed a molybdenum-zinc-chromium-activated clay catalyst which was packed in a continuous bed in each of four converters with four internal tubes per converter to introduce cooling hydrogen at suitable points in the beds. (See drawing no. 6) The feed averaged 14 cubic meters of oil plus 30,000 cubic meters of gas per hour, with an additional 7-8,000 cubic meters of gas for temperature control in the converters. The reaction temperature was approximately 500° C. and the operating pres-

DRAWING No. 6

(This drawing has been inserted in an envelope
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5.   Description of Gas Phase Operation (b)(cont'd.)

sure was 700 atmospheres. The equipment and method of opera-
tion, 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 re-
quired to produce a suitable reaction velocity. At 500° C.,
however, the equilibrium was unfavorable for complete hydro-
genation, so that the resulting gasoline was rich in aroma-
tics. 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 vari-
ous phases of the hydrogenation process consisted of satur-
ated hydrocarbons methane to butane and higher, carbon diox-
ide, carbon monoxide, ammonia, and hydrogen sulfide to-
gether 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 de-
pended 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 inter-
mediate expansion stages (50 atm.) of the cold and inter-
mediate separator oils and circulating gas stream scrubber
liquid were usually used for fuel directly. Since they con-
tained 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