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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 S_2 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

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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 converter and temperature measurements were taken at the entrance 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. Between 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 millimeters high of tungsten disulfide. This material was prepared 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 became 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 cracking 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 [redacted]ED

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.

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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 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-

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

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 moleculer 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

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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 5058 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-

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DRAWING No. 6

(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 (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

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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 Alkazid treatment to remove hydrogen sulfide and carbon dioxide from the gases. The Alkazid process consisted in "scrubbing" the gases with an alkaline solution of either alanine or glycocol 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, conteining phenols, hydrogen sulfide, carbon dioxide, and ammonia, was usually treated with either tricresyl phosphate or phenolsolvan solution to remove the phenols in the same menner as aqueous liquors from coking plants. Then the water was given an Alkazid treatment to remove the hydrogen sulfide before discharging to avoid polution 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 [redacted] 80602

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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 is 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.

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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-

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7. Sump Phase Solids Removal and Oil Recovery (a)(cont'd.)

cipitated some of the heavier asphalts so that they could be removed from the system. Combinations of these methods were used depending upon the existing conditions at the plant, but in any case it was always necessary to thin the viscous slurry prior to centrifuging.

After dilution the slurry passed to continuous centrifuges where it was separated into an oil containing 6 to 10 percent finely divided solids, and a heavy residue containing 35 to 40 percent solids. The ash content of the solids in the oil averaged about 35 percent, the balance of the solids being asphalt type constituents and fusain. The solids in the residue contained about 50 percent ash plus the major fraction of the unconverted coal. The centrifuges employed were commercial machines, many of them made by DeLaval, which operated on the automatic solid ejection principle. The inside diameter of the housing was about 480 millimeters and the vertical rotating shaft carried about 200 perforated conical disks spaced about one-half millimeter apart. The rotor turned at about 3200 r.p.m. so that a very high centrifugal force of about 10,000 times gravity was obtained. Tungsten carbide valves were employed at the residue discharge to resist the abrasion of the solids. The slurry capacity of these machines was approximately 2.5 tons per hour so that a coal hydrogenation plant had a large battery of them handling the hot separator product.

The lack of complete removal of the solids in the centrifuges was caused by the relatively viscous medium, the low density difference between some of the solids and the oil, and the extremely fine size of many of the particles. The operation of the centrifuges was a compromise between through-put and completeness of purification, since longer contact times resulted in more complete elimination of the solids. It was necessary to remove the residue as a thick slurry in these machines, since too thick a sludge caused the automatic discharge valves to become fouled. This method of centrifuging divided the feed into approximately two-thirds recycle oil and one-third residue, and the large amount of oil in the latter material constituted

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7. Sump Phase Solids Removal and Oil Recovery (a)(cont'd.)

a heavy load on the sludge coking plant. The Germans realized the liabilities in the process, had done some research work on the problem, but had apparently not found a better solution.

In 1938 the Leuna plant of the I. G. Farbenindustrie conducted tests on the filterability of the slurries using three different types of equipment, a Wolf cell filter, a cartridge filter, and a Dorr rotary filter.(25) The cartridge type unit gave the highest filtering rate of about 130 kilograms of slurry per square meter per hour, while the cell filter averaged 100, and the Dorr machine only 50. The solids content in the pasting oil, the washing of the filter cake, and the wash oil requirements were most favorable with the cartridge filter. The results of these tests, however, were not sufficiently attractive to warrant the installation of filter equipment in the new hydrogenation plants built in 1940-1943.

(b) Coking of Centrifuge Residue.

As previously mentioned the residue from the centrifuges contained 60 to 65 percent oil, which if it had been discarded, would have been a serious loss. It was therefore necessary to further treat the sludge in order to recover the oil content for recycle in the system. This operation was carried out in coking ovens where the material was heated and the oil distilled off leaving a dry, high ash residue which could be burned by mixing with fresh coal.

The sludges from brown coal, which were low in asphalt were frequently processed in a screw type oven. See drawing no. C-12 for construction and operation of this unit. The apparatus consisted of a gas-fired furnace which contained two steel drums each about one meter in diameter by 16 meters in length, so supported, one over the other, that the upper drum discharged into the lower drum. The feed inlet to the upper drum and the coke discharge from the lower drum were at one end of the unit and the inter-connection between the two drums at the other end. Inside of each drum was a screw that turned at about one revolution

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7. Sump Phase Solids Removal and Oil Recovery (b)(cont'd.)

per minute. In the lower part of the furnace a set of steam superheater coils were located. Auxiliaries consisted of a feed pump, and a traveling rake to remove the solids as they were discharged from the lower section of the kiln. The gases and vapors evolved were freed from dust, and were then cooled. The condensed oil was recovered in a series of heat exchangers and coolers, and collected in settling tanks. The gaseous products were used for fuel.

In operation the sludge was pumped through a heat exchanger counter-current to the outlet oil, gas, and water vapors before it entered the oven. Ordinarily the warmed material entered the hollow shaft of the top screw, and passed through the length of the oven where it was discharged into the drum. It was possible, however, to inject the feed directly into the kiln, should the lines become stopped up with material. Superheated steam equivilant to 5-10 percent of the charge was injected into each tube to lower the partial pressure and reduce cracking of the oil. After the residue had been moved by the screw from the inlet end to the rear of the top drum, it dropped down into the lower drum and was carried forward until it finally was discharged into a sump where it was cooled by water. A traveling rake then carried it out and loaded it into cars for disposal.

The oil vapors, gas, and steam together with a small amount of dust left through a connection at the rear of the kilns. The dust was removed in a cyclone separater and was discharged by gravity into a water sump and was pumped or carried away for disposal. The gaseous products were next partially cooled in the heat exchanger by the feed material, and then in to a water cooler. The condensate from these two units was a heavy oil suitable for recycle as a pasting medium. A light oil as well as most of the water vapor was condensed in an after cooler using water and the noncondensable gases were used for heating purposes. The light oil, after separation from the water was sent to the distillation building and blended with the sump phase overhead product to recover an additional quantity of middle oil.

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7. <u>Sump Phase Solids Removal and Oil Recovery (b)(cont'd.)</u>

The operating temperature of the oven was about 550°C, and its through-put was approximately two tons of sludge per hour. About 75 percent of the oil was recovered. The major difficulty in operation was coking up of the screws especially in the lower tube. Usually the on-stream time was about 100-120 days for the top section and only 17 to to days for the bottom between cleanings. These furnaces would not handle high asphalt content feeds on account of coking of the screws. Even with relatively good feed stocks the operating time was quite short between maintenance periods.

In order to handle the sludges from bituminous coal hydrogenation plants, a combination ball mill rotating oven was employed. This apparatus consisted of a large drum about two meters in diameter by 11 meters long inclined at about 6° from the horizontal, and mounted in a gas fired furnace. See drawing no. C-13 for flow details of this type of system. The mill oven was lined with high chrome abrasive-resistant steel and held about 9-10 tons of balls. The feed and part of the steam were injected through pipes in the hollow trunnion at one end, and the remaining steam was introduced at the opposite end in a similar manner. The vapors left through the trunnion at the feed end of the oven. The solid coke was removed at the end opposite the feed and collected in a water-sealed sump. In the upper section of the furnace setting were coils for superheating steam and also for preheating the feed. The auxiliaries were essentially the same as those employed for the screw type furnace, the dust collector and the heat exchanger being combined into one unit.

The operating temperature was usually a little higher, about 560-590°C, than that used for the screw coking oven, but the oil recovery was essentially the same. About 10-15 percent of steam was added to the charge to reduce cracking and gas loss. These ovens coked up in about five days of operation, but due to the grinding action of the steel balls they were self cleaning by merely shutting off the feed and continuing the rotation for 10-12 hours.

The sludge through-put was considerably greater than

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7. Sump Phase Solids Removal and Oil Recovery (b)(cont'd.)

in the screw-type furnace, 3.2 tons as compared with 2 tons per hour. Another big difference was the much lower oil content in the residue, about 1-2 percent as compared with 20-25 percent. The higher temperature produced more gas so that the overall oil recovery was essentially the same. It was of interest, however, that the ratio of heavy oil to light oil was greater in the ball oven than in the screw type, despite the fact that the gas yield was almost double. The ratios of heavy to light oils were 4.8 and 3.4, respectively, from the two units operating on the same feed.

Table No. 8 in Appendix A contrasts the operation of these two types of furnaces.

8. Description of the T.T.H. Process.

The T.T.H. process or Tief-Tempratur Hydrierung (low temperature hydrogenation) represented a markedly different approach to the hydrogenation of coal tar to obtain diesel fuel and lubricating oils. In 1935 experimental work was started on the problem of preparing lube oils from brown coal tar by means of a limited hydrogenation so as not to destroy the paraffinic nature of the tar. By 1938 the work had reached the stage for commercial application, and in 1939 the first and only plant in Germany was started at Zeitz.

The feed for the process consisted chiefly of brown coal tar from low temperature carbonization with about 10 percent of light oil added. The raw tar contained about 0.5 percent finely suspended dirt and 0.4 percent water which were largely removed by centrifuging. The clarified tar was next filtered and the dirt content reduced to a maximum of about 0.01 percent. An analysis of the tar feed showed that it contained 83.4 percent carbon, 10.5 percent hydrogen, 2.0 percent sulfur, 0.4 percent nitrogen, and 3.7 percent oxygen. The specific gravity at 50°C was about 0.95, and analytical distillation showed that 6 percent boiled up to 180°C, 33 percent up to 325°C, and 52 percent up to 350°C.

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8. Description of the T.T.H. Process.(cont'd.)

The equipment in which the conversion was conducted was essentially the same as that used in the gas phase hydrogenation. The hot equipment was located in a stall which held two heat exchangers, an electric preheater and three catalytic converters. The Zeitz plant had five of these stalls operating on the T.T.H. process during the war. Since the equipment was nearly the same as that previously described, only those items which were different will be discussed.

The reaction occured in the liquid phase over an active catalyst at between 300 and 390°C. under a total pressure of 300 atmospheres. A partial pressure of hydrogen of about 85 percent was maintained at the converter inlet, but at the outlet it had dropped to about 80 percent. The through-puts were relatively low averaging 0.35 and 0.4 tons of tar per cubic meter of catalyst per hour. In a three converter system having 25 cubic meters of catalyst, the tar through-put was therefore about 9-10 tons per hour. Approximately 25,000 cubic meters of gas per hour were mixed with the tar and heated in the exchangers and preheaters, while an additional 14,000 cubic meters were required for temperature control in the converters. The hydrogen consumption was approximately 550 cubic meters per ton of tar.

A hot separator was not used in this system, even though it was a liquid phase process since there were no solids to be removed. The whole product was collected in the cold catch pot and distilled.

The converter design was a little different from that employed in the gas phase, although the general features were similar. (See drawing no. C-14 in Appendix C). A forging 1000 millimeters in diameter by 18 meters long was insulated and lined as was done with both the sump and gas phase reactors. Only one grating, similar to that used in the gas phase converter was installed in the lower section so that the catalyst bed was continuous instead of being divided into sections. The catalyst volume was increased to 8.4 cubic meters by this means. It was still necessary to introduce cooling gas to control the reaction temperature,

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8. Description of the T.T.H. Process (cont'd.)

so six down pipes located at strategic points were used. A ring with holes around the circumference was connected to the lower end of each of the cooling gas pipes and used to distribute the gas throughout the catalyst bed. As in the gas phase reactors the thermocouple well was located in the center.

A rising flow of oil and gas were employed in the converters, since the velocities were not as great as in the other hydrogenation processes and the liquid phase tended to cushion the catalyst and reduce attrition. The catalyst most frequently used, when available, was no. 5058 tungsten disulfide pellets, the same as used in prehydrogenation. The complete preparation of this material is given in Appendix B. When tungsten became scarce, the substitute catalyst No. 7846W250, sometimes referred to as 8376, was used. This latter material was a mixture of 25 percent tungsten sulfide plus 3 percent nickel sulfide on activated alumina. As mentioned in Section V under the prehydrogenation process, this catalyst was very active in reducing oxygen and nitrogen compounds as well as hydrogenating the lower boiling constituents, but it was less effective in cracking and hydrogenating higher boiling materials. The milder cracking was desirable, but the reduced hydrogenation activating was a liability, so that altogether the Germans felt that 5058 catalyst was the better material to use whenever available.

The average catalyst life depended very greatly upon the purification of the feed tar. As previously explained, the dirt content was reduced to about 0.01 percent by centrifuging and filtration, and great care had to be exercised to keep this dirt value low. This suspended solid matter would gradually foul the catalyst surface together with condensed polymerization products that could not be desorbed. Soluble ash, such as iron phenolate, also caused trouble by being reduced and deposited on the catalyst surface. The only way to avoid the latter difficulty was to choose feed tars that contained very little soluble inorganic compounds. If proper precautions were taken, a catalyst life of six months to one year was obtained. Regeneration of the catalyst in *situ* was not possible, but instead fresh material was charged,

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8. Description of the T.T.H. Process.(cont'd.)

and the active ingredients recovered at the catalyst plant.

The purpose of the process was to very carefully refine the high molecular weight paraffinic substances without cracking and destroying them, so that they could be recovered as lube oils and waxes. For this reason the low temperature was absolutely necessary, as the lube oil fraction decreased rapidly above 390°C and at 420°C it practically disappeared being converted into gasoline and diesel oil. Under actual condition approximately 80 percent of the fresh tar was converted into desired products with the following distribution: 27 percent gasoline, 43 percent diesel oil, 5 percent lube oil, 9 percent wax, 0.5 percent $C_3 + C_4$ gas, and 14 percent residue which could be processed in a sump phase tar hydrogenation plant.

The gasoline, as produced, was not useable directly, but had to be further treated in either the gas phase plant or in a DHD process. Its average composition was 5 percent aromatics, 30 percent naphthenes, and 65 percent paraffins, and consequently the octane rating was low, about 55. The diesel oil fraction boiled from 200 to 320°C and had a cetane rating of 45-50. Its composition was similar to that of the gasoline, but it was a satisfactory fuel as produced, whereas the gasoline was not. The phenol and sulfur contents averaged 1 percent and 0.1 percent, respectively.

After removing the gasoline and diesel oil cuts, the residue oil was vacuum distilled to produce lube oils. The total lube oil fraction had a VI of 60 to 80, but it was usually fractionated to produce a spindle oil and a machine oil. The relative yields were approximately two-thirds of 4° Engler spindle oil and one-third of 6 to 8° Engler machine oil.

The waxes were extracted from the residue by means of the conventional propane process. These were divided into soft and hard wax. The former constituted about one-third of the product with a melting point of 40-45°C: the latter two-thirds with a melting point of 52°C. These waxes were used for the production of fatty acids, or were cracked

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8. Description of the T.T.H. Process.(cont'd.)

and the olefines polymerized to make lubricating oils.

A complete report of the operation of the T.T.H. process including actual yields for 1944 at the Zeitz plant was obtained, and further information on the process, if desired, may be obtained from this document.(27)

9. Description of Pott-Broche Process.

Although this method for treating coal was more like a solvent extraction than a hydrogenation, however, its similarity in operating conditions and its use in conjunction with coal hydrogenation plants makes this report the logical place for presentation. Briefly, the theory of the operation was to contact finely ground coal with a suitable solvent at a temperature and pressure high enough to dissolve a major portion of the coal. The untreated coal and ash were removed by filtration and the solvent recovered by distillation leaving a high molecular weight coal extract which could be fed to a coal hydrogenation plant to produce fuels.

In 1927 research work on the commercial application of solvent extraction to bituminous coals was started by Drs. Pott and Broche. The work progressed slowly, but by 1934 it had reached the point where it was deemed advisable to build a pilot plant for testing the process on a larger scale. In 1936 the Ruhröl A.G. constructed the first commercial unit with a capacity of 26,000 tons per year of bituminous coal extract. On account of difficulties and peculiarities in the process, which will be discussed later, this was the only plant built and operated in Germany for coal extraction.

The feed material was Ruhr bituminous coal which had a moisture content of 5-10 percent and an ash content of 5-7 percent. On a dry, ash-free basis the coal contained 86.7 percent carbon, 5.1 percent hydrogen, 1.2 percent sulfur, 1.6 percent nitrogen, and 5.4 percent oxygen. The volatile matter content averaged 27-28 percent, which was

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

markedly lower than the 38 percent obtained from bituminous coals used in nearby hydrogenation plants. The coal was dried to 0.5 to 1.0 percent moisture content, and then ground in ball mills so that 95 percent was finer than 100 mesh, and about 65 percent was finer than 250 mesh. See drawing no. 8 for process flows.

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

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

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DRAWING No. 8

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

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9. <u>Description of Pott-Broche Process (cont'd.)</u>

bitumens and fusain.

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

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

The slurry of coal solution and solids after leaving the reaction chamber was filtered to remove the solids. Three ceramic cartridge filters containing about 35 elements each were employed to filter the slurry at 150°C and six atmospheres differential pressure. The filter medium was a poraus stone annular ring, about 125 by 80 millimeters in diameter by 33 millimeters thick. Approximately 60 of these were mounted on tubes, and so arranged in the filter

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

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

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

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

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

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

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

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

10. Discussion of the Products of Hydrogenation.

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

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

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10. Discussion of the Products of Hydrogenation (cont'd.)

by the three step hydrogenation process for coals and tars, the two step hydrogenation process for pitch as practiced at Welheim, and the two step hydrogenation of coals and tars followed by a DHD treatment. The last mentioned operation was becoming increasingly important in Germany from 1939 until the close of the war, and for further details on this subject the reader is referred to U. S. Naval Technical Mission in Europe Report entitled "The Manufacture of Aviation Gasoline in Germany."(24)

The following table shows the principal characteristics of aviation gasoline produced by the first two methods from brown coal, brown coal tar, bituminous coal, bituminous coal tar, and pitch.

TABLE I

CHARACTERISTICS OF AVIATION GRADE GASOLINE BY HYDROGENATION

Raw Material	Brown Coal	Brown Coal Tar	Bituminous Coal Tar	Bituminous Coal	Pitch
Approximate yield, tons/ton*	0.42	0.72	0.75	0.47	0.23
Specific Gravity, 15°C	0.72	0.71	0.73	0.74	0.78
Distillation:					
Initial °C	45	48		46	
% to 70°C	25	17		15	
% to 100°C	67	64	65	58	38
% to 120°C	89	88		78	

*Includes only the coal processed in the high pressure Sump Phase.

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TABLE I (cont'd.)

Raw Material	Brown Coal	Brown Coal Tar	Bituminous Coal Tar	Bituminous Coal	Pitch
% to 150°C	--	--		96	
E.P.°C./1%	139/98	134/98	160	151/98	165
Vapor Pressure, atm.	0.39	0.42		0.50	0.45
Composition:					
% Paraffins	52.5	58.0	37	36.5	35
% Aromatics	8.5	10.5	8	9.0	45
% Naphthenes	38.0	30.5	55	54.0	20
% Unsaturates	1.0	1.0	--	0.5	--
Octane No.(Motor Method)	71	69	76	73	80
Octane No.(+.12% T.E.L.)	90	89	94	91	95

This table shows the relatively high paraffin content of the gasolines produced from brown coal and brown coal tar and the resultant lower octane ratings compared with those produced from bituminous coal and pitch. The yield of gasoline from bituminous coal was also greater on account of the lower oxygen and higher carbon content. Coal tar of course gave the highest conversion to gasoline, while the high asphalt content of the pitches made it more profitable to sell a major portion of the surplus product as fuel oil instead of recycling. The aviation gasoline produced, however, had a very good octane rating on account of its high aromatic and isoparaffin contents.

The German fuel program for the war required consider-

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10. Discussion of the Products of Hydrogenation (cont'd.)

ably more aviation gasoline than motor fuel, and only 25-30 percent of the total gasoline production from the hydrogenation plants was motor fuel grade. Since bituminous coals were superior raw materials for aviation gasoline, those plants processing that material produced only aviation gasoline. Part of the production of the brown coal and brown coal tar plants went to motor fuels, as the high paraffin contents of the oils gave them lower octane ratings. Then, too, it was more difficult to produce a high quality material in the single gas phase treatment of brown coal tar. The following table shows the principal characteristics of motor gasolines.

TABLE 2

CHARACTERISTICS OF MOTOR FUEL BY HYDROGENATION

Raw Material	Brown Coal	Brown Coal Tar
Approximate yield, tons/ton	0.47	0.80
Specific gravity, 15°C	0.77	0.74
Distillation:		
Initial °C	35	43
% to 70°C	21	15
% to 100°C	45	38
% to 120°C	61	57
% to 150°C	81	85
E.P. °C/%	191/98	168/99
Vapor pressure, atm.		0.63 at 40°C
Composition:		
% Paraffins	59.0	56.0

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TABLE 2 (cont'd.)

Raw Material	Brown Coal	Brown Coal Tar
% Aromatics	8.5	17.0
% Naphthenes	30.5	26.5
% Unsaturates	2.0	0.5
Octane No. (Motor Method)	60.5	about 60
Octane No. (+.12% T.E.L.)	about 75	

Some diesel oil was produced by hydrogenation of brown coal and brown coal tars, since the high paraffin contents of the oil gave it a good cetane value. Only the sump phase plus the first gas phase hydrogenation were employed, as the object was to obtain a product high in normal paraffins and naphthenes. The TTH process gave a high conversion of brown coal tar to diesel oil which had the same characteristics as that made by the two stage hydrogenation.

TABLE 3

CHARACTERISTICS OF DIESEL OIL BY HYDROGENATION OF BROWN COAL AND BROWN COAL TAR

Specific Gravity	0.84
Aniline point, °C	45
Distillation:	
Initial °C	194°C
% to 220°C	33
% to 240°C	55
% to 260°C	72
% to 280°C	84

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TABLE 3 (cont'd.)

E.P. °C/%	312/99
Phenol	less 1%
Sulfur	less 0.1%
Cetane NO	45-50

The T.T.H. process using brown coal tar was the only combination of raw material and hydrogenation processes that was used to produce lube oils and waxes, as direct hydrogenation destroyed the paraffin constituents in the other coal substances processed. The Zeitz plant produced two grades of lube oils, a light 4° Engler (180 SSU) spindle oil and a heavy 6-8° Engler (215 SSU) machine oil. The yields were approximately two parts of the former to one of the latter. The waxes were also of two grades, a hard wax and a soft wax. The former, which had a melting point of 40-45°C, constituted one-third of the production, while the other two-thirds had a melting point of 52°C.

Fuel oil was produced in limited amount almost exclusively by the hydrogenation of pitch. As has been previously mentioned, the high asphalt content of the heavy residue oil from the sump phase distillation would have been difficult to hydrogenerate, if it had been recycled. Therefore, this product was sold for fuel oil. The yield of fuel oil was approximately twice that of gasoline. The Welheim plant (Ruhroel AG) was the only large unit to operate on pitch.

11. Operation and control of the Units.

(a) Introduction.

This section of the report deals with mechanical operation of the equipment. It will include a summary of operating sequence for starting up and shutting down the high pressure chambers, safety measures, an outline of control methods, and a brief discussion of instrumentation. Operations which are common to all chemical industry, such as

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11. Operation and Control of the Units (a)(cont'd.)

operation of pumps and compressors will not be covered except for conditions peculiar to this particular process.

(b) Sump Phase Starting Procedure.

Before a new sump phase unit is first put into operation, all masonry and internal insulation must be dried. This ordinarily requires about two days at 120°C, during which time nitrogen is pumped through the system. Instrument checking and servicing requires about 8 hours.

The entire sequence of starting up is as follows:

(1) Purge system with nitrogen, after purging is complete, build N_2 pressure to 300 atm. and check for leaks. It is important that nitrogen be used, not only to avoid explosive mixtures within the equipment, but also to prevent fires in case there is leakage in the piping or equipment.

(2) Expand N_2 to 50 atm, using the excess for testing other equipment.

(3) Start gas circulators.

(4) Dry out preheater masonry.

(5) Check all meters and instruments.

(6) Blow down the nitrogen and fill the system with circulating gas at 300 atms.

(7) Put meters and instruments into service.

(8) Start heating the system with 12,000 m^3/hr of circulating gas, of which about 1/6 goes through the heat exchangers. The temperature at the inlet to the first converter is slowly increased at a rate of about 15 - 18°C per hour.

(9) When the temperature reaches about 300°C the slurry of oil and catalyst (30 percent of catalyst) is

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11. Operation and Control of the Units (b)(cont'd.)

started to the preheater at a rate of 1000 liters/hr, rapidly increasing to 3000 liters. At the same time about 1000 liters per hour of oil are started through the heat exchangers.

(10) Start up the hot oil circulating system at 2000 liters/hour, increasing to 6000 - 7000 liters in about 30 minutes.

(11) When the separators are filled to the normal operating level, the expansion valves are used to hold this level.

(12) As the temperature rises, the use of fresh oil increases, and when it amounts to 6000 - 7000 liters/hour the catalyst slurry is turned through the heat exchangers.

(13) Turn cooling water on slowly.

(14) Control temperature out of the heat exchangers by increasing gas through-put.

(15) The rate of temperature rise is the system is slowed down as the normal operating temperature is approached.

(c) Shutting Down a Sump Phase Unit.

(1) Drop temperature at a rate of 15 - 18° per hour. Cut back on fresh feed, at the same time leaving the gas through-put and circulation unchanged.

(2) Stop catalyst addition at 425°C.

(3) Hold the cold separator temperature constant, unless the product becomes too viscous.

(4) When temperature reaches 250 - 220°C all heat can be removed from the preheater and the flue gas blower shut down. The combustion chamber is purged with nitrogen, and if the shut-down is to be of long

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11. Operation and Control of the Units (c)(cont'd.).

duration the fuel lines are blanked off.

(5) All oil circulation and fresh feed is stopped at 165 - 185°C. The preheater is flushed with oil, then blown out with nitrogen. The chambers must remain hot enough to permit complete removal of the sludge.

(6) Gas circulation is contained for 10 minutes, then shut off. The liquid is blown out in sequence from the hot separator, the converters 4 to 1, and the regenerator. The gas is blown down through the expansion valve, taking care that the pressure difference across the entire unit does not exceed 15 atm.

(7) Purge the system with nitrogen for about 50 minutes until no more than 5 percent combustible is found in the outlet.

(8) Blank off all connections to the apparatus to be repaired.

(d) Starting a Gas Phase Unit with Electric Preheater.

(1) Test the electrical system with about 20 volts from the transformer, checking the resistance by comparison of voltage and amperage.

(2) Flush the system with nitrogen to 0.5 percent maximum oxygen.

(3) Build up nitrogen pressure, increasing the pressure from 1 to 20 atm in 1½ hours, and from 20 to 300 atm in 2 more hours. This slow buildup is necessary to protect the catalyst pellets from destruction caused by unbalanced pressures inside and outside the pores, and from damage by physical disturbance from excessive gas velocities. Check all piping for leaks. 30 atm. is sufficient pressure for this purpose if the unit has previously been in operation.

(4) The gas circulator cannot be operated with N_2 over 50 atm because of its greater density compared to

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11. Operation and Control of the Units (d)(cont'd.)

H_2. Drop the pressure to 50 atmospheres slowly, then start the circulator.

(5) Blow off the nitrogen to other equipment, and fill with circulating gas. Care must be taken to prevent overheating of the catalyst as heat is released during adsorption of H_2. The pressuring velocity must not exceed that given above for nitrogen.

(6) Start the circulator when the pressure is up to normal, and circulate about 10,000 m^3/hr.

(7) Heat up the inlet to the first converter at a rate of about 10° per hour.

(8) When the temperature is 220°, open the cold hydrogen valves to the converters, and check the temperature at each inlet point to be certain that the lines are clear and the cold gas is actually entering the converter. Start the oil feed at a rate of 1 to 2 m^3 per hour per converter, checking its progress through the system with the temperature elements. Put water on the coolers.

(9) Control the temperature to the first converter by adjusting the cold hydrogen to the feed. If necessary, the current can be shut off of the preheater.

(10) Increase the oil feed by about 500 liters per hour to a value of about 7 m^3 per hour.

(11) If the temperature in the converter falls off much when the oil feed is started, cut the feed in half and increase the heat. Otherwise a sudden reaction may overheat the chamber with a high oil throughput.

(12) Hourly samples of the oil at the pump and at the separator should be taken for specific gravity determination. If the gravity increases suddenly the feed must be reduced or cut off until an explanation is found. Too heavy oil or water in the feed will permanently damage the catalyst.

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(13) As the converter temperature approaches the normal range, gradually increase the hydrogen and oil feeds to the unit to full volume.

(e) Shutting Down a Gas Phase Unit.

(1) Cut back the feed by 2-3m^3/hour, holding the catalyst temperature constant until all oil feed is stopped.

(2) Reduce the inlet temperature to the first converter by about 10-12°C per hour.

(3) Follow the procedure of liquid removal and gas expansion as outlined for the Sump Phase.

(f) Temperature Control in the Converter.

If the temperature rises in some part of a gas phase converter, the normal control is increase of the cold gas injection at that point. If the temperature shows signs of going out of control, and this condition is verified by the gas density recorder, as many of the following steps are taken in sequence as are necessary to bring the temperature under control:

(1) Heat is cut off of the preheater.

(2) Oil feed is shut off.

(3) Gas circulation temperature is decreased, and if this does not suffice, gas feed is cut off.

(g) Operating Safety.

Equipment or piping that has been removed from service is always carefully tested before operation is again undertaken. This testing includes hydrostatic tests of 1½ times the normal working pressure on equipment that has been repaired, leakage tests on heat exchangers, converters and piping systems. The entire system is tested with nitrogen at the working pressure of the unit before hydrogen is

11. Operation and Control of the Units (g)(cont'd.)

turned in. The flushing and purging procedure has been mentioned in the preceding pages.

The large high pressure equipment is installed in concrete cells enclosed on all sides, but with a removable door for installation or removal of equipment. The walls extend to the top of the vessels, and there is no roof. This arrangement has protected the operators and as far as is known no one has ever been hurt in the control room by an accident or explosion in the cell. However, the cells are so close to buildings on the opposite side from the control room, where the door is located, that on one occasion an explosion in the cell killed seven men in the coal paste pump building. A disadvantage of the cells enclosed on four sides is that explosions of gas in the cell are much more violent than if one side were open. On several occasions the converters have been blown or have fallen out through the door of the chamber. The open construction with only one main fire wall, as at Billingham England, appears to be much more desirable, but of course requires more space both for the cells and for the protective area in front of the cells.

An emergency blowdown system was installed in most of the plants. This arrangement was intended as a method of minimizing bomb damage, but is also useful in case of accident. The liquid is drawn off to an underground receiver from which the gas is vented to the air.

The following list of accidents in high pressure plants since 1930(38) shows only the major incidents, and is probably not complete, but it will give an idea of the causes and results of failures.

Plant	Year	Description
Leuna	1930	One chamber (cell) destroyed by failure of an S2 tube which had been installed in a hot location.

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11. Operation and Control of the Units (g)(cont'd.)

Plant	Year	Description
Leuna	1935	Expansion machine cylinder failed, killing one man, shutting down the plant completely for two weeks and partially for three months
Scholven	1937	Dust explosion in the coal drying plant.
Nordstern	1940	Preheater fire, due to splitting of an N10 return bend.
Nordstern	1940	Preheater explosion due to plug on a return fitting blowing out.
Nordstern	1940	Fire in a sump phase chamber due to destruction of an emergency blowdown line following failure of a checkvalve and a blow down valve.
Nordstern	1940	Building explosion in the CO_2 absorption plant caused by operating failure of a level indicator on the absorber and breakage of a line to the expansion machine--Due to thawing out the equipment during extremely cold weather--One death.
Nordstern	1940	Leakage in the circulating system caused by foundation sinking.
Pölitz	1940	Gas was accidentally turned into a cell under repair. Explosion followed, killing three.
Pölitz	1941	Circulating gas line plugged with hydrate, causing overheating of the converter. Two converters were blown out of the chamber by the explosion.

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11. Operation and Control of the Units (g)(cont'd.)

Plant	Year	Description
Pölitz	1942	Gas inlet line plugged off, overheating converters. The resulting explosion blew two converters out of the cell, and a flame 30 meters long followed. Seven men in the upper part of the coal paste pump house opposite the cell were killed.

It will be noted that most of the accidents occurred when the various plants were new, and could possible be traced to inexperienced operators.

Chart No. 1 on the following page shows the frequency of cell fires in Leuna from 1927 to 1940. An examination of this chart will show that the curve increases with the increasing size of the plant until 1929, when operating experience and development of improved alloys and better design brought a sharp decrease. The increase in 1934 is probably again due to plant expansion. The fires in the last several years amount to only about two a year for all units.

In conclusion it should be emphasized that widely spaced units with cells open on one side would prevent the majority of series accidents. Cell and preheater fires, while spectacular, rarely cause serious damage to equipment or injury to personnel in the Billingham plant of I.C.I. which uses this principle.

(h) Control and Control Instruments.

Free use was made of indicating and recording instruments in the coal hydrogenation plants, particularly of temperature instruments. Automatic control was much less extensive, and only in the last four or five years has it been used to any large extent. The automatic control instruments were all specially built and were usually of somewhat crude design when compared to industrial instruments of the United States. A brief description of the use and operating principle of the various instruments is given below.

11. Operation and Control of the Units (h)(cont'd.)

The "Ringweage" (Fig. 1) was almost universally used for fluid flow indication or recording.(40) The primary element is an orifice plate or flow nozzle installed in the line in the usual way. The "Ringwaage" merely shows the differential pressure across the orifice, which is proportional to the square of the flow for any given installation. The Leeds and Northrup "Centrimax" and possibly other American makes operate in a similar manner. The instrument was used to record all gas and clean oil flows necessary for material balances or for control, such as fresh hydrogen, circulating gas, cold gas to each point, and the various product gases and liquids.

The coal paste charge quantity was determined by measurement of the stroke velocity of the pump. The instrument (Fig. 2) records an average velocity every three minutes. The "Eckhardt" piston displacement meter was used for some liquid measurements, and utilized a similar mechanism for recording the flow.

Coal feed to the paste mixer and catalyst feed to the slurry were weighed on "Dosierbandwaagen" (Fig. 3) which was a rather conventional automatic scale.

Pressure indication is by gauges with heavy steel spiral bourdon tubes, or by dead weight piston gauges. The piston gauges can be spring loaded or pendulum weight loaded. Accuracy of a fraction of an atm at 700 atm pressure was claimed for some of these instruments.

A differential pressure recorder (Fig. 4) was used to determine pressure drop across various parts of the system during operation. These were sometimes installed with remote oil-controlled valves so that they could be easily switched from one service to another. The photograph shows a piston instrument showewhat similar to the pressure instrument described above. Another type which was sometimes used operated with two steel coil bourdon tubes controlling air pressure through a moveable nozzle. The air pressure was proportional to the pressure difference and was recorded. A gas density instrument (Fig. 5) operating on the Bunsen law principle recorded two gas densities on

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11. Operation and Control of the Units (h)(cont'd.)

the same chart. It was usually applied to the inlet and outlet gas from the reaction chamber, thus giving the operator a picture of the condition of the process. A similar instrument was usually installed on all important metered gas flows where change in density might occur. These data are necessary for accurate measurements.

A combustion apparatus (Fig. 6) could be used for various purposes, such as determination of oxygen in the gas or combustible gas in the air. It contained a catalyst which caused oxidation and the amount of combustion is indicated by the recorded temperature of the outlet gas from the reaction.

A newer type of magnetic oxygen recorder (Fig. 7) has been developed which will indicate 0.01 percent oxygen in the gases. It makes use of the great magnetic susceptibility of oxygen by passing the gas mixture between the poles of a powerful electromagnet, then over a resistance differential thermometer which shows a temperature effect if oxygen is present. The only gas which has a magnetic susceptibility comparable to oxygen is NO, therefore this gas must be absent or the quantity must be accurately known. Further development envisions a permanent magnet instead of the 100 watt D.C. electromagnet.

An H_2S recorder (Fig 8) is operated on the conductivity change of a cell containing a solution of bromine or cadmium chloride. The scale could be made for any concentration of H_2S down to 10^{-5} or 10^{-6} volume percent. The reactions involved are shown on the figure. The second reactant ($CdCl_2$) is usable in the presence of unsaturated hydrocarbons, as the first (Br) is disturbed by the presence of HCN, NO, NH_3 or unsaturates. This instrument was used mostly in the gas separation units.

Ultra red absorption instruments$^{(41)}$(Fig 9, 10) used to analyze for methane, CO, etc, operated on the small temperature difference between the methane-containing gas and pure methane when they were exposed to ultra red rays from the same source. This instrument is known in the U.S., and according to the I.G. staff the American type is much

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better than their own.

The most important class of instruments was probably that for indicating, recording or controlling temperature, and very free use was made of this type in the hydrogenation plant. The extent of this use can best be demonstrated by the following photostats of drawings 1675 and 1677 which show the pressure and temperature points of the chamber and the preheater, respectively, of Sump Phase Chamber 5 of the I. G. Leuna Plant.(42) In the coal chamber the elements were iron constantin thermocouples, and because the temperatures are often given in millivolts for this couple in the literature and documents, a conversion chart is shown here. The type of each preheater element depends on the temperature at the point of installation. The report entitled "Fortschritte auf dem Gebiete der Messung, Regelung und selbsttätigen Betriebüberwachung von Hochdruckanlagen" in the appendix describes briefly some of the German methods and experiments for increasing accuracy and speed of thermometric instruments. They claim an accuracy of ± 1 or 2°C in their measurements at 400° to 500°C, using photoelectric cell compensators.

The Pölitz and Gelsenberg plants use a temperature alarm instrument that covers 60 points in less than two minutes, but the older plants rely primarily on indicating instruments which are switched from one point to the other, with only a few points of major importance recorded automatically.

Liquid level instruments(43) are of two types, both of which are used in the U. S. One uses the differential pressure, recorded on a "Ringwaage", due to the hydrostatic pressure when very small flows of gas are bled into two tubes, one of which opens above the liquid surface and the other of which extends to a point near the bottom. This instrument was used for the hot separator of the sump phase, and for other services where heavy or dirty products were handled.

The second is the well-known displacement type where the buoyant effect of the rising level decreases the apparent

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11. Operation and Control of the Units (h)(cont'd.)

weight of a suspended cylinder.(44) The Germans supported the cylinder on a coil spring so that an iron rod attached to the top of the cylinder rises into an induction coil with rising level. The increasing insertion of the iron rod changes the inductence of the coil which can be determined and recorded as proportional to the liquid level. The Brown electric flow meter in the U. S. uses a similar principle, one advantage of which is the complete absence of any packing or stuffing box. This instrument was used for cold separators, column kettles, etc. where the liquid was fluid at atmospheric temperature and was comparatively free from sediment or suspended matter.

Automatic control of variables in the high pressure coal hydrogenation plants is in its infancy in Germany, and as mentioned before, the design of the instruments is somewhat crude when compared to American practice. Electric, pneumatic, and combinations of the two types of control are utilized. The controlled valves are usually of the diaphragm type, often using balanced pressures on both sides of the diaphragm rather than spring loading in one direction. A crude form of valve positioner was developed to overcome the stuffing box friction which is invariably present in high pressure control valves. Some hydraulic valves were observed, but these were usually remote manual control valves rather than automatic. Solenoid valves were also built, but their use in large sizes was not frequent.

The automatic controls in the Leuna plant were as follows:

(1) Liquid level, cold separator.
(2) Temperature into first converter.
(3) Temperature into second converter.
(4) Liquid level, intermediate separator.
(5) Temperature control of desanding first sump phase converter.
(6) Liquid level, hot separator.
(7) Liquid level, oil feed storage.

Not all of these instruments were used on all units,

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and they are arranged in order of decreasing numbers. A description of the controls and their applications is included in the appendix in a report "Selbsttätige Regelung der Sumpf-und Gas phase Kammern in der Hydrierung des Leunawerkes."

(i) High Pressure Joints and Closures.

There are no indications that any novel or improved joints or closures for high pressure vessels or piping have been used in the German High Pressure Coal Hydrogenation Industry. The flanged piping joints used screwed, through-bolted flanges, and the gaskets were lens rings very similar to standard American high pressure practice. The lens rings were usually made of the same material as the pipe, and the joint was a line contact between the ring and the ground end of the pipe itself.

No self-sealing gasket designs were found. The large vessel closures all had the bolts in tension, and the entire gasket load was taken by the bolting. The bolts and nuts were usually made from one of the S steels for 325 atm. service, and from one of the K steels for 700 atm. service. Bolts were studded into the end of the vessel and passed through drilled holes in the forged head, with the nuts on top of the head.

Two general types of large vessel closures were found. The simpler type had no separate gasket, but the tapered end of the head entered the vessel and wedged the stainless steel liner of the vessel against the vessel wall. This design is shown on drawings C-1, C-5, and C-10 in the appendix to this report. The second type of closure uses a separate steel ring which has a facing of 1mm thick pure aluminum on the seating surfaces. The seating surfaces are bevelled at a 30° angle so that the aluminum is wedged into a recess in the head on the head seating surface and between the head and the vessel wall on the other surface. A detail of this construction is shown on drawing C-4 in the appendix, and the equipment shown on drawings C-7, C-11, and C-14 uses the same general design. Apparently

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11. Operation and Control of the Units (1)(cont'd.)

the separate gasket is used only when the vessel has no stainless steel liner.

12. Materials of Construction.

One of the great problems in high pressure high temperature processes of any kind is the development or selection of construction materials that will stand up under the operating conditions. For coal hydrogenation the primary requirements of materials for the high pressure equipment are:

(1) Hydrogen resistance at high temperature and with high hydrogen partial pressure.
(2) High tensile and creep strength at the operating temperature.
(3) Resistance to H_2S and Cl_2 corrosion.

A great amount of experimental and development work has been done in Germany in an effort to produce suitable steels, but at best a compromise must be made between the various properties listed above. Their problems were multiplied by wartime shortages of molybdenum, tungsten, and chromium. Austenitic 18-8 Cr-Ni steel was fairly satisfactory, but the tonnage were so great that Germany could not supply the high chromium and nickel requirements.

The early experimental work on the hydrogenation process was done with vessels of various carbon steels, but hydrogen attack was severe and the vessels failed in a very short time.(31) Low alloy chrome nickel steels were then used, but nickel appeared to decrease the hydrogen and H_2S resistance of the alloy. Molybdenum was then substituted for nickel, and gave better alloys with less alloying metal. About 0.5 percent Mo gave high temperature strength properties equivalent to 2.0 percent Nickel. Krupp P469 (N6) was the first steel of this type. In chronological order, steels N6, N8, V 2AED, and N10 were developed, each being an improvement over previous material for high temperature high pressure hydrogen service. Then, during the war, N 8V and N9 were used to save critical alloys, but were not nearly so resistant to corrosion as the earlier steels.

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12. Materials of Construction. (cont'd.)

Attached diagram 652 from the IG Farbenindustrie Ludwigshafen Works presents some of the characteristics of the materials mentioned. The "Dauerstandfestigkeit" is the maximum load at which the elongation does not exceed 0.001 percent per hour in a period of 25-35 hours after the beginning of the test, and the total elongation does not exceed 0.2 percent after 45 hours.

The steels used in the hydrogenation plant were classified according to general type and the purpose for which each was used.

Table I, at end of this report, lists the manufacturers, chemical analyses, physical properties, heat treatment and field of usefulness of the various steels of each group.

"S" steels are ordinary carbon steels. They do not withstand high temperature or hydrogen attack, but they are useful for flanges, bolts, cold piping and fittings, lens rings, gaskets, and structural supports. There appears to be little new in the "S" steels either in manufacture or in application.

"N" steels are the high temperature steels and are the most important group. The structural steels, NO, NOS, NO4, N2, CV, are characterized by about 1 percent Cr content and are used for stressed pieces which are not directly in contact with hydrogen or corrosive materials.

The N1 and N5 to N10 alloys contain more Cr, usually 3 or 6 percent and are the hydrogen resistant group of the low alloys. The heat treatment of this group is quite critical, and consists of heating to the austenitic region, quenching, and annealing. These steels have great mechanical strength at high temperature and are resistant (but by no means immune) to chemical attack.

N-1 steel is used almost exclusively for pressure vessels containing hydrogen, but it is not suitable for use at temperature above 250° C, because above this range hydrogen does attack the carbon and weaken the grain boundaries. For this reason all high pressure, high temperature vessels

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12. Materials of Construction. (cont'd.)

of this material contain internal insulation or cooling surfaces to maintain the shell at a lower temperature than the process materials.

N6 was the first preheater tube material that could be used to replace 18-8 Cr-Ni steel.(34) It was not entirely satisfactory due to low creep strength and a low resistance to hydrogen attack, but some N6 preheater tubes were still in service in Leuna during the war.

N8 was first used about 1935. It is a 3 percent Cr alloy with ½ percent tungsten, and is cheaper as well as stronger than N6 at the preheater operating temperature. N8 has somewhat lower high temperature strength than 18-8 Cr-Ni steel, and requires particularly careful heat treatment, but it is still considered satisfactory for 325 atm. preheater tubes.

N10 steel(35) is the best low alloy material that has been found for high temperature hydrogen service, and all preheater tubes and fittings for 700 atm. service were made from it. Exceptionally high hydrogen resistance and creep strength were claimed. It has more vanadium and less chromium, molybdenum, and tungsten than N8, thus a saving was made of the most critical metals during the war. Most of the newer installations had N10 preheater tubes whether they operated at 325 atm. or at 700 atm. except where wartime necessity required the use of substitutes. If N10 is properly heat treated (heated to 1050°, cooled in air stream, anneeled at 700°) the cold tensile strength can be 90-100 Kg/mm^2. Faulty heat treatment can produce a material brittle at room temperature but still satisfactory at 500-600° C. Air stream cooling in the quench gives a Brinell hardness of 220-260 compared to 240-280 by oil quench, but the Germans state that the air-cooled steel has almost twice the strength at 500-600° C of oil quenched steel in that temperature range.

N10 steel preheater tubes were in service for five years before a failure occurred that could not be traced to some manufacturing flaw. Up to that time they had considered the metal immune to hydrogen attack, but they found that

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12. <u>Materials of Construction. (cont'd.)</u>

a very slow removal of carbon from between the grains did occur. It has been claimed that a heat treatment of the tubes after each period of not more than 10,000 hours service will prolong the tube life indefinitely. This heat treatment is presumably the same as the initial treatment.

N steels can be arc or resistance welded but gas welding is risky. The design of most large vessels avoids welding but resistance welding of preheater tubes and piping is regular practice. The welding procedure most be followed by heat treatment.

"K" steels were made primarily for 700 atm work where the "S" steels were not sufficiently strong. The "K" steels contain about 1 percent Cr, and have lower Mo and higher C than the S steels.

The remainder of the steels shown have counterparts in American practice. The "RA" steels are 18-8 Cr-Ni alloys for acid and chemical resistance. The "RM" steels are 12-14 Cr steels for hardened pieces such as valve parts. 25Cr 20 Ni alloys are the non-oxidizing, flame-resistant steels. Alloys containing 1-5 percent nickel are used for heavy duty forgings such as piston rods, and for low temperature service. The final groups are the surface hardening and nitriding steels.

Hydrogen sulfide corrosion becomes progressively more severe as the temperature rises. Under the pressure and temperature conditions of coal (or tar) hydrogenation H_2S attack on ordinary carbon or low chrome steels is quite rapid. For instance, the Billingham plant of I.C.I. uses 1½" thick low chrome steel liners in the converters and they estimate their life at about 5 years. The hydrogen sulfide cannot be eliminated because it forms during the conversion and because it is necessary to have some of this gas present to preserve the sulfide catalyst used in gas phase operation. A 14 percent chrome alloy withstands the conditions imposed, but due to the difficulty involved in fabricating large pieces from this material the Germans sometimes made their liners for converters and hot separators from 18-8 Cr-Ni steel.

12. **Materials of Construction (cont'd.)**

It was found that brass containing at least 37-42 percent zinc has very high H_2S resistance, but of course brasses cannot be used at the high temperatures involved. In one set of German experiments they made a series of iron-zinc and nickel-zinc alloys containing up to 50 percent zinc to see if such alloys would be H_2S resistant. (It is interesting to note that these alloys were made under 60 atmospheres nitrogen pressure because of the high vapor pressure of zinc at the melting point of iron or nickel.) Alloys containing as much at 15 percent zinc were not attacked by H_2S but, as might be expected, the alloys were too brittle to be of any practical use. However, these experiments led to the vapor galvanizing of parts such as heat exchanger tubes and liners, a procedure that apparently proved to be satisfactory and is still used. They also galvanized 13 percent Cr converter internal parts. The vapor galvanizing is accomplished by holding the parts in zinc vapor for 25 hours at 870°C., thus forming a very thin crust of Fe-Zn protective alloy.

Chlorine and chlorine compounds form some hydrochloric acid under the conditions of hydrogenation. No practical construction material will withstand this attack, therefore when chlorine is present in the feed, soda ash is added to neutralize the acid.

Erosion is a serious problem in much of the equipment and piping. It can be traced to one or the other of two sources in most instance. One source is abrasive material in suspension in the fluids being processed, such as ash, sand and catalyst in the coal paste, the sump phase liquids, and in the sludge recovery system. Wear in the paste pumps is combatted by using surface hardened metals and nitrided plungers and valves, and by low plunger velocity. The return bends of the sump phase preheaters suffer much damage and hardened inserts, usually of 12-14 percent chrome steel, are often placed inside the outer wall of the fitting. Valves have hardened seats and discs, and are designed so that the flow is streamlined as much as possible. Heat exchanger tube sheets are approached with long conical sections which reduce solid deposition as well as erosion on the ends of the tubes. Stuffing boxes are equipped with

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12. Materials of Construction. (cont'd.)

flushing oil connections, and are flushed continually while in service.

The second type of erosion is due to high flow velocities of fluids, especially mixtures of vapor and liquid, through pressure release points. This condition is partially combatted by the design of the unit and the equipment. Expansion is carried out through expansion engines or in several stages. Expansion valves have turbulence chambers with slightly restricted openings on the outlet. Piping is installed undersized in order to take part of the pressure drop. Where it is necessary that a considerable pressure drop be taken across a valve, the seat and disc are made replaceable and of some abrasion resisting material such as tungsten carbide or tungsten-titanium carbide. Two pressure reducing stations are always installed in parallel, with shutoff valves one each side of each expansion valve so that it can be removed from service for replacement or repairs.

Hydrogen attack on steels(37) is a particular type of corrosion, causing decarburization at the grain boundary, and it is of such great importance in high temperature high pressure operation that it is considered seperately. The mechanism of the attack is the slow hydrogenation of the carbon in the steel to methane. This takes place primarily in the matrix rather then in the crystals, and greatly diminishes the strength of the steel. The reaction velocity for any given steel increases with the temperature and with the hydrogen partial pressure. The resistance of steels to hydrogen attack varies from that of carbon steel, which is quite sensitive even at 200°C, up to stabilized 18-8 Cr Ni austenitic alloys which are practically immune over the entire range of temperature used in the process.

Due to the great cost of austenitic stainless steel, low alloys were developed which would have sufficient hydrogen resistance for particular purposes. These are the "N" steels. N4 could be used for 325 atm H_2 up to 400°C and N6 and N8 up to 600°C. The use of 700 atm pressure dropped these permissible temperature ranges and forced the development of N10.

12. **Materials of Construction. (cont'd.)**

The first report of tests published by F.K. Nauman in 1938 (Stahl und Eisen, pg 1239) stated that N10 was unaffected by 200 atm hydrogen at 600°C in 100 hours. The failure by hydrogen attack of N10 preheater tubes after several years of service caused additional study of the effect. It was found that chemical analysis alone did not mean much with regard to hydrogen susceptibility, but fabricating and operating conditions played a considerable part. Many steels showed evidences of attack only after 400-600 hours and some only after 1000 or more hours. Heat treatment was an important factor, and in general, air quenched steels were found to be more resistant than oil quenched. These tests indicated that resistance increased with a decrease in unstable carbides in the matrix and with less dissolved carbon in the ferrite, also, that complete immunity is not attained by ferritic-pearlitic steel containing as high as 6.5 percent Cr., but that grain boundary failure will occur in time.

The following four figures show micrographs of N10 tubes which failed in 700 atm. service in the hot section of a preheater after approximately 11,000 hours service. The two photographs with a magnification of 12 diameters show the fissures caused by hydrogen attack which ultimately result in failure of the tube. These fissures are typical of hydrogen attack on any steel. The two micrographs with a magnification of 125 diameters emphasize the deterioration at the surface in contact with the hydrogen. The etched sample in particular shows the effect of the decarburization on the steel grain structure.

The following figure shows bend tests of samples taken from one of the tubes which failed. The samples from left to right are taken: from the inner tube surface, with the immediate surface removed, 0.2 mm removed, 1 mm removed, middle of tube, outside of tube. It can be seen that the attack penetrated less than one millimeter over the tube as a whole.

Results of experiments led the Germans to believe that the life of N10 steel preheater tubes could be prolonged indefinitely by giving them a heat treatment after each

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12. Materials of Construction. (cont'd.)

10,000 hours service. Apparently the heat treatment reestablished the carbon equilibrium in the steel of the inner tube surface, but it is not clear just how this was accomplished.

A thorough study of the use of columbium to replace the carbon for blocking grain slippage in the steel was proposed as a possible method of developing a completely hydrogen resistant low alloy steel. These experiments were not carried out due to wartime shortage of manpower.

The German creep strength test consists of putting a series of constant loads on test pieces held at the specified temperature for periods of 45 hours each. The creep strength (Dauerstandfestigkeit) is the greatest load in Kg/mm^2 at which the creep velocity does not exceed 1/1000 percent per hour during the 25-35 hour period and the total extension in the 45 hours does not exceed 0.2 percent. It is claimed that this test is reproducible and extremely useful as a method of evaluating creep strength in a short term test.

A second method of evaluating high temperature strength is a plot of different constant loadings at constant temperature against the number of hours elapsing before the fracture of a given material occurs. This is known as the load-time curve (Belastungs-Standzeitlinien), and is usually plotted on both rectangular and log-log coordinates. Two types of these plots are shown in the attached figures. The first two (marked Abb. 4 and 5) show curves for a 0.91 percent Ni, 0.78 percent Cr, 0.94 percent Mo steel at 300°, 400°, 500°, and 600° C., plotted with the two types of coordinates. The second pair shows the curves for 500° C of five different chrome steels, including V2AE, N9, a 20 percent Cr. steel and two low alloy Cr-Ni steels.

The following figure (Abb. 18) shows the loading, time to fracture, elongation, and reduction in area beneath photographs of test pieces of a steel corresponding to N10 composition which were broken under the various loads. It is interesting to observe the changing appearance of the

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12. Materials of Construction.(cont'd.)

fracture after increased periods of time. The next figure shows the relation between the break point and the loading which produces an elongation of 0.2 percent after various periods under tension at 500°C. The poor qualities of wartime substitute N9 as compared to N10 are plainly shown.

The following tables are taken from Technical Report No. 87-45 of the U. S. Naval Technical Mission in Europe, and shows the uses of the principal materials in high pressure equipment.

It should be noted that N8 and N9 would both be replaced by N10 for new construction when alloying metals are available in the necessary quantities.

Internal parts and liners for the vessels are not listed above, but austenitic 18-8 Cr-Ni still is the preferred material, with 18 percent Cr steel as the best substitute.

Austenitic stainless steel is also preferable for pressure shells, but N1 is satisfactory when precautions are taken to avoid metal temperatures of over about 250° C. It can be noted that no cases of failure of pressure shells have been found, although on a few occasions vessels have been blown out of the cells by gas explosions in the cell space.

On the whole, the German development and selection of steels appear to be satisfactory in conjunction with their equipment design.

(b) Insulation(39)

There were three principal classes of service where insulation was required in the high pressure hydrogenation units. The first consisted of coverings for pipe lines and fittings; the second was the internal insulation employed inside of the pressure vessels to maintain the shell temperature below 250° C; and the last was the protection of steel work to prevent buckling in case of fire.

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12., Materials of Construction (b)(cont'd.)

For pipe coverings in the range of 100 to 250° C, an insulation called Diamag, which was a Magnesium carbonate, Kieselguhr, asbestos mixture in a 60 - 25 - 15 ratio, was employed. This material was used for low pressure steam lines and pipes which were not carrying very hot fluids. In the temperature range of 400 - 450° C. glass wool or rock wool was commonly used on hot gas and high pressure steam lines. A sheet metal housing outside of the pipe was packed with the wool to a density of about 180 kg/m^3 for glass wool and 240 kg/m^3 for rock wool. At these densities the respective thermal conductivities at 200° C were 0.063 and 0.956 KCal./meter (hr)(°C.).

At temperatures over 450° and up to 300° C a diatomit insulation was used. This material was a kieselguhr produced by a low temperature burning. It had a compression strength of 6-8 kg/cm^2, a density of 450 kg/m^3 and a thermal conductivity of 0.08 Kcalories/meter(hr)(°C) at 100° C. An asbestos cement of 4 percent asbestos, 90 percent kieselguhr and 6 percent alumina plus a binder was commonly used to fill in the cracks and produce a smooth surface. When the lines were to be protected against possible fires, a thin iron sheath was placed on the outside of the insulation and held in place by galvanized iron bands.

As has been previously described, the inside of the hot, high pressure vessels such as the converters, heat exchangers, and hot separators were insulated in order to keep the external wall temperature below 250° C., and thereby prevent hydrogen embrittlement. A harder grade of Diatomit made by burning kieselguhr at a higher temperature was used for this purpose. The compression strength of the Diatomit blocks was 25 kg/m^3, and the thermal conductivity was 0.12 K. Cal/meter(hr)(°C.) at 100° C. At 200-300 atmospheres pressure the conductivity of the oil saturated Diatomit rose to 0.4 - 0.8 k.Cal/meter(hr.)(°C.). In practice the vessels were lined with blocks of the insulation about 65 m/m thick, and asbestos cement was employed to fill up the cracks. The cement had a thermal conductivity essentially the same as that of the Diatomit.

In order to protect the structural steel work in the

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12. Materials of Construction (b)(cont'd.)

stalls from buckling in the case of fire, the supports for the converters and connecting girders were insulated. A layer of Diatomit blocks about 65 m/m thick was laid around the outside of the structural steel and held in place by a wire mesh. A coating of 15-20 m/m of cement was applied over the top to protect against weather and to make a smooth finished surface. Other structural steel members were also covered with either brick or Diatomit and finished with a cement coat. These precautions helped to prevent more serious accidents in the case of fires, since the steel could stand intense heat for 30 minutes or longer when so protected.

The following table No. IV shows the I.G. Farbenindustrie application of various types of insulating materials for different applications. The ordinates show the temperature ranges and the services, while the blocks show the type of material and the thickness for different diameters.

13. Conclusions.

In a planned economy and in anticipation of war, a nation may artifically stimulate the production of potentially strategic materials. In this light the chronological development in Germany of the high pressure hydrogenation processes are of interest. The earliest commercial plants were the Haber units for the hydrogenation of nitrogen to ammonia. Developed prior to 1913, this process made Germany independent of Chile saltpeter imports for explosives production during World War I.

The experience gained in design and operation of these units proved helpful when the Germans expanded their search for materials and started in the early 1920's to hydrogenate carbon monoxide to methanol. The designs of auxiliaries, safety precautions, and materials of construction could be applied directly, and the designs of the converters, heat exchangers, and separators, could, with suitable modification, be used. Thus the Germans had two large scale high pressure processes in operation prior to the next expansion

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13. Conclusions. (cont'd.)

in 1926 when the first coal hydrogenation plant was started at Leuna. Here again much of the early work on ammonia and methanol was applied directly; however, this operation, involved the handling of solids, and it was necessary to gradually evolve specialized equipment such as converters, preheaters, and heat exchangers. This latter operation was much more difficult than the straight handling of gases and clean liquids as in the ammonia and methanol systems. New techniques were developed and the high pressure stage changed so that either coal or tar could be handled in the same equipment. A second, gas phase hydrogenation was developed that could process middle oil from any of several sources to produce a variety of motor fuels. Thus in the two stage hydrogenation process the Germans had a fairly flexible process capable of handling a wide variety of raw materials to produce end products of nearly the same characteristics or widely different, as desired.

Mention has been made of the enormous size of these plants in relation to their throughputs. The largest plants were Leuna and Bruex each of which produced approximately 600,000 tons of motor fuel per year. Each used ten to twelve high pressure stalls with all of the auxiliaries, such as gas manufacture, gas purification, power and steam production, gas compression and recycle units, product treatment, and covered an area of roughly fifteen square kilometers. It is difficult to evaluate the cost of these German plants on account of an arbitray relationship between the reich mark and the dollar. An indication may be obtained from a proposal made by the I.G. Farbenindustrie to the U.S.S.R. in 1939 giving the cost of a plant to produce 180,000 annual tons of aviation gasoline by the hydrogenation of brown coal.(28) The total cost of the high pressure plant and all auxiliaries was estimated at 47,800,000 R.M. Since this production corresponds to only 4,000 barrels a day, the cost per barrel per day is 12,000 R.M. At a 40 cent R.M. this corresponds to an investment of approximately $5,000 per barrel of aviation gasoline per day. This investment is high, and the operating cost would also be quite high on account of the large amount of labor required. Automatic controls were virtually unknown, as compared with

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13. Conclusions. (cont'd.)

American practice, and instead manual operation was used in all but the simplest positions. Undoubtedly American engineering and instrumentation could materially cut the labor requirement, but it would still be a major item. The utilities also formed a large fraction of the operating cost. For every ton of bituminous coal processed, it required approximately four or five tons to supply the power, steam, and hydrogen.

In anticipation of and during the course of war, the present Germany again resorted to high pressure hydrogenation to produce certain materials regardless of cost. With little petroleum accessable, Germany planned to use other raw materials, such as coal, to supplement the meager supplies of crude oil obtainable from outside sources. Altogether eleven large installations were constructed for processing coal and tar with a total production of aviation gasoline (the principal product) in 1942 of about 3,900,000 tons or 32,000,000 barrels per year. While relatively large and a tribute to German engineering this output was entirely too small to support the war needs of Germany and was further diminished by strategic bombing during the later war years.

The high pressure hydrogenation of hydrogen-poor materials as developed by the Germans was a very interesting process from the scientific viewpoint. The possibilities of altering the compositions and/or quantities of various materials by changes in operating conditions or catalyst naturally attracted the interest of technical men. The economy of the process, however, was not so easily determined. The huge investment cost and the large number of men required to operate a plant that would produce 13,000 barrels per day (output of the largest units) made for high production costs. For a country that did not have any appreciable supply of petroleum, a high pressure plant could possibly compete in a protected home market. In the United States with its still large reserves of low-cost petroleum the process at present could not hope to make headway without a subsidy. Outside of small scale experiments in government supported laboratories such as the Bureau of Mines, and certain research institutions like Armour Research Foundation and Battelle Memorial Institute, there are

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13. <u>Conclusions.(cont'd.)</u>

no known applications of coal hydrogenation to produce gasoline or liquid fuels in the United States.

Certain phases of the hydrogenation process might be considered to advantage, since it is highly probably that they might soon become economically feasible. The Standard Oil Company of New Jersey is conducting a limited hydrogenation of lube oils in order to saturate them and improve the viscosity index, but this is practiced only on a very small and limited scale. This company at its Baton Rouge refinery has also conducted many tests on the hydrogenation of cracked residues to obtain an additional yield of gasoline. This work is still in progress, and has reached the point where an increase in the price of either crude or gasoline will make the process economically attractive. The Standard Oil Company has followed the development of high pressure hydrogenation for many years, learning much of the technique from the I.G. Farbenindustrie. It is now in a position to exploit the process as soon as the economics are favorable.

Another point in favor of hydrogenating residues is the conservation of crude reserves. For every barrel of gasoline obtained from residuum about two barrels of crude may be left in the ground. Obviously the marketing of residues as fuel oil is only done because of the low selling cost of gasoline. Therefore, the furthbr investigation of the advisability of processing these heavy hydrogen-poor materials in stages such as the Germans used for tars might well be considered.

Along the same line it might be economically feasible to process the heavy ends of crude petroleum in order to increase the hydrogen content before cracking. Such measures would raise the yields of gasoline per barrel of crude and at the same time decrease the amount of residue to be either reworked or sold. Undoubtedly the two processes could be advantageously worked together so that a heavy fraction from the crude petroleum would be blended with the cracking recycle stocks and hydrogenated, the ultimate products being only gasoline and gas.

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13. <u>Conclusions.(cont'd.)</u>

In conclusion it does not appear that coal hydrogenation as practiced by the Germans offers any immediate prospect of competing with petroleum in the United States. It is quite possible, however, that certain features of the process may soon become justified from both a conservation and economic standpoint. The work of the Germans should be carefully studied by any industry undertaking to exploit any phases of high pressure operation. Such a study should be of considerable help in the design and operation of high pressure plants.

Prepared by:

JOHN H. HOWELL
Technician.

ROY M. CRAWFORD
Technician.

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APPENDIX A

TABLES OF OPERATING DATA

TABLE NO. 4

Analysis of German Coals Used For Hydrogenation.

Type of Coal	Brown Coal		Bituminous Coal	
Plant	Leuna	Wesseling	Gelsenberg	Pölitz
% Ash in dry coal	12.8	5.9	3.0	6.6
Element Analysis on dry, ash-free basis				
% C	71.9	68.7	83.8	81.9
% H	5.7	5.0	5.3	4.9
% O	17.9	24.9	8.0	11.5
% N	1.0	1.3	1.75	1.1
% S	5.8	0.40	1.0	0.8
% Cl	----	0.11	0.09	0.05
% available H	4.1	2.4	4.6	3.9
Volatile Matter	57.9	53.5	37.5	37.2

TABLE NO. 5

Summary of Operation Data for Sump Phase Hydrogenation

Material Treated	Brown Coal	Brown Coal Tar	Bituminous Coal	Pitch
Temperature, °C	470-480	450-460	485	485
Pressure, atm.	300&700	300	700	700
Catalyst	Iron Oxide	Iron sulfide	Sodium Sulfide Iron Oxide Iron Sulfide	Iron Sulfide
Total reaction volume per stall, in M^3	27	27	36	36

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TABLE NO. 5 (cont'd.)

Material Treated	Brown Coal	Brown Coal Tar	Bituminous Coal	Pitch
Specific feed rate tons/m^3 hr	1.1 - 1.3	0.75	0.9 - 1.0	0.7
Total feed rate, tons/hr	30 - 35	20	33 - 37	25
Concentration of material in feed, wt. %	36 - 40	75	40	60
Total gas flow, M/hr	35-45,000	27,000	50,000	40,000
Gas Circulated with paste, M^3/hr.	25-30,000	20,000	30,000	25,000
Gas used for cooling, M^3/hr	10-15,000	7000	20,000	15,000
Water added to product, M^3/hr.	1	1	1	0.7
% Conversion of Coal	97	-	95	----
Tons of middle oil/ton feed	0.48	0.38	0.62	0.29
Tons of C_3 plus C_4/ton feed	0.06	0.03	0.12	0.02
Hydrogen Consumed /ton middle oil, M^3	1500	250	1600	700-800

TABLE NO. 6

Analysis of Sump Phase Oils

Middle Oil From	Brown Coal	Bitminous Coal
Specific Gravity 20°C	0.962	0.974
Aniline point Phenol-free oil, °C.	-10	-20
% Phenolics	20	15
Element Analysis		
% C	36.05	87.28

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TABLE NO. 6 (cont'd.)

Middle Oil From	Brown Coal	Bituminous Coal
Element Analysis		
% H	9.37	9.54
% O	3.90	3.08
% N	0.55	1.06
% S	0.13	0.04
gms H / 100 gms. C	10.90	10.93
Heavy Oil from		
Specific gravity, 50°C.	1.030	1.038
Element Analysis		
% C	88.62	39.27
% H	8.40	8.26
% O	2.62	1.64
% N	0.28	0.77
% S	0.08	0.06
gms H/100 gms C.	9.46	9.25

TABLE NO. 7

Summary of Operating Data for Gas Phase Hydrogenation

Stage	Prehydrogenation	Gasoline Production Coal & Tar	Pitch
Temperature, °C	390-410	400-420	500
Pressure, Atm.	300	300	700
Catalyst	Tungsten Disulfide	Tungsten Dissulfide & Act. Clay	Chrome-Zinc Malybdenum Act. Clay
Total Catalyst volume per stall, M^3	28	23	32
Specific feed rate, tons/M3 hr.	0.6-0.8	1.2	0.45

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TABLE NO. 7 (cont'd.)

Stage	Prehydrogenation	Gasoline Production Coal & Tar	Gasoline Production Pitch
Total feed rate, tons/hr	20	35	14
Total gas flow M3/hr	55,000	27,000	38,000
Gas circulated with oil, M3/hr	35,000	20,000	30,000
Gas used for cooling M3/hr	20,000	7,000	8,000
Tons gasoline produced /ton feed/pass*	0.20	0.60	0.50
Tons C3 plus C4/ 1 ton feed/pass*	0.08	0.075	0.12
Hydrogen consumed/ton middle oil, M3	500	200	950

TABLE NO. 8

Comparison of Screw Type with Ball Type Sludge Coking Ovens

Type of Oven	Screw		Ball	
Plant	Wesseling	Leuna	Wesseling	Gelsenberg
Steam Consumption tons/ton feed	6.5	19.5	15.5	20.0
% solids in moisture free product	75.5	81.0	99.5	96.2
% ash in solids	86.2	83.0	64.2	41.1
% Benzol soluble oil in discharge product	24.5	19.0	0.5	3.8
Coke analysis of moisture free product				
% tar	6.1	8.7	0.5	1.3
% Coke	93.2	91.3	99.4	95.0
Ash content of the coke	70.8	75.2	64.4	42.0

*Single pass through the Converters Yields.

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TABLE NO. 9

Element Balance for Sump Phase Operation with Brown Coal

	Total Tons	Carbon Tons	Hydrogen Tons	Oxygen Tons	Nitrogen Tons	Sulfur Tons	Residue Tons
Dry Brown Coal	1000.00	619.12	48.06	181.93	5.81	53.72	91.36
Catalyst	89.48			61.53			27.95
Fresh Gas H_2	52.95		52.95				
N_2	13.94				13.94		
CO	3.03	1.30		1.73			
CO_2	2.48	0.68		1.80			
CH_4	5.76	4.31	1.45				
Total Fresh Gas	78.16	6.29	54.40	3.53	13.94	-	-
Total Inlet	1167.64	625.41	102.46	246.99	19.75	53.72	119.31
Middle Oil	417.17	353.98	44.24	14.84	1.68	2.43	
High Volatile Gasoline	19.73	16.42	3.31				
Total Liquid Product	436.90	370.40	47.55	14.84	1.68	2.43	
Outlet Gas H_2	7.29		7.29				
N_2	13.94				13.94		
CO	13.27	5.69		7.58			
CO_2	91.26	24.90		66.36			
CH_4	37.68	28.20	9.48				
C_2	31.80	25.40	6.40				
C_3	36.41	29.75	6.66				
C_4	19.39	16.02	3.37				
C_5	2.90	2.41	0.49				
H_2S	34.66		2.05			32.61	
Total outlet Gas	288.60	132.37	35.74	73.94	13.94	32.61	-
Miscellaneous Solids in Sludge	214.13	18.01	0.72	38.99	0.67	21.00	134.74

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TABLE NO. 9 (cont'd.)

	Total Tons	Carbon Tons	Hydrogen Tons	Oxygen Tons	Nitrogen Tons	Sulfur Tons	Residue Tons
Water of Reaction	148.25		16.59	131.66			
Phenols	2.18	1.67	0.14	0.37			
H_2S in Disch. H_2O	1.21		0.07			1.14	
NH_3 in Disch. H_2O	3.21		0.57		2.64		
CO_2 in Disch. H_2O	4.49	1.22		3.27			
Oil Lost in Coking	75.05	70.50	4.18	0.27	0.05	0.05	
Total Miscellaneous	448.52	91.40	22.27	174.56	3.36	22.19	134.74
Total Outlet	1174.02	594.17	105.56	263.34	18.98	57.23	134.74
Balance Difference	+ 6.38	-31.24	+3.10	+16.35	-0.77	+3.51	+15.93
Balance Difference in % of Inlet	+ 0.54	-5.00	+3.02	+ 6.62	-3.90	+6.53	+12.93

TABLE NO. 10

Element Balance for Sump Phase Operation with Bituminous Coal

	Total Tons	Carbon Tons	Hydrogen Tons	Nitrogen Tons	Sulfur Tons	Oxygen Tons	Residue Tons
Dry Coal	1000	769	45.0	11.3	5.2	107.7	61.8
Catalyst	44.8		1.4		2.7	20.8	19.9
Pasting Oil	1363	1239.3	99.5	10.6		13.6	
Solids in Pasting Oil	117.4	72.5	2.6	0.8	2.9	0.7	37.9
Heavy Oil Added	63.9	57.7	5.2	0.4		0.6	
Flushing Oil	52.0	46.8	4.3	0.4		0.5	
Fresh Gas(1,150,000M^3)	140.0	14.6	95.7	29.3		0.4	
Total Inlet	2781.1	2199.9	253.7	52.8	10.8	144.3	119.6

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TABLE NO. 10 (cont'd.)

	Total Tons	Carbon Tons	Hydrogen Tons	Nitrogen Tons	Sulfur Tons	Oxygen Tons	Residue Tons
Middle Oil	526						
Cold Separator Oil		965.3	91.4	8.0	0.3	24.0	
Heavy Oil	563						
Phenol Oil	3.7	2.8	0.3			0.6	
Oil in Slurry	922	844	62.5	8.1		7.4	
Solids in Slurry	294	138.3	5.9	1.2	7.6	1.7	139.3
Slurry Gas	30.1	14.6	8.0	5.5		2.0	
Lean Gas	146	79.7	34.4	21.8	0.5	9.6	
Rich Gas	166.7	123.5	31.4	4.8	0.8	6.2	
Reaction Water	96		10.7			85.3	
NH_3 in Water	6.8		1.2	5.6			
H_2S in Water	0.2		0.0		0.2		
CO_2 in Water	8.9	2.4				6.5	
TOTAL OUTLET	2763.4	2170.6	245.8	55.0	9.4	143.3	139.3
Balance Difference	-17.7	-29.3	-7.9	+2.2	-1.4	-1.0	+19.7
Balance Difference in % of inlet	-0.64	-1.34	-3.12	+4.16	-13.0	-0.70	+16.5

TABLE NO. 11

Element Balance for 5058 Gas Phase Operation with Brown Coal Middle Oil

	Total Tons	Carbon Tons	Hydrogen Tons	Oxygen Tons	Nitrogen Tons	Sulfur Tons
Middle Oil	1102.98	935.8	116.92	39.26	4.52	6.40
High Volatile Gasoline	27.04	22.51	4.53			
H_2S	3.36		0.20			3.16

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TABLE NO. 11 (cont'd.)

		Total Tons	Carbon Tons	Hydrogen Tons	Oxygen Tons	Nitrogen Tons	Sulfur Tons
Fresh Gas	H_2	52.34		52.34			
	N_2	13.70				13.70	
	CO	3.14	1.35		1.79		
	CO_2	2.61	0.71		1.90		
	CH_4	5.62	4.21	1.41			
Total Fresh Gas		77.41	6.27	53.75	3.69	13.70	
Total Inlet		1210.79	964.66	175.40	42.95	18.22	9.56
Gasoline		1000.00	858.32	139.46	0.94	1.14	0.14
Outlet Gas	H_2	3.25		3.25			
	N_2	11.84				11.84	
	CO	0.22	0.09		0.13		
	CO_2	0.92	0.25		0.67		
	CH_4	9.21	6.89	2.32			
	C_2	2.92	2.33	0.59			
	C_3	27.38	22.37	5.01			
	C_4	81.82	67.62	14.20			
	C_5	0.89	0.74	0.15			
	H_2S	2.44		0.14			2.30
Total Outlet Gas		140.89	100.29	25.66	0.80	11.84	2.30
Miscellaneous							
Water of Reaction		45.13		5.05	40.08		
Phenol		2.13	1.63	0.14	0.36		
NH_3 in Disch. H_2O		5.78		1.03		4.75	
H_2S in Disch. H_2O		6.45		0.38			6.07
CO_2 in Disch. H_2O		1.06	0.29		0.77		
Total Miscellaneous		60.55	1.92	6.60	41.21	4.75	6.07
Total Outlet		1201.44	960.53	171.72	42.95	17.73	8.51
Balance Difference		-9.35	-4.13	-3.68	--	-0.49	-1.05
Balance Difference in % of Inlet		-0.76	-0.43	-2.10	--	-2.69	-10.98

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TABLE NO. 12

Element Balance for 5058 Gas Phase Operation

with Bituminous Coal Middle Oil

	Total Tons	Carbon Tons	Hydrogen Tons	Nitrogen Tons	Sulfur Tons	Oxygen Tons
Middle Oil	1000	863.8	108	4.9	4.3	19.0
Fresh Gas 489,000 M^3	59.4	6.2	40.5	12.5		0.2
Total Inlet	1059.4	870.0	148.5	17.4	4.3	19.2
Gasoline	360					
Cold Separator Oil		852	131.9	0.1		
Middle Oil	624					
Phenol Oil	0.4	0.3				0.1
Lean Gas	31.4	8.5	12.6	9.8		0.5
Rich Gas	7.8	5.6	1.5	0.5	0.1	0.1
Reaction Water	18.1		2.1			16.0
NH_3 in Disch Water	7.7		1.4	6.3		
H_2S in Disch Water	6.2		0.4		5.8	
CO_2 in Disch Water	0.4	0.1				0.3
Total Outlet	1056.0	866.5	149.9	16.7	5.9	17.0
Balance Difference	-3.4	-3.5	+1.4	-0.7	+1.6	-2.2
Balance Difference in % of Inlet	-0.32	-0.40	+0.95	-4.0	+37.3	-11.5

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TABLE NO. 13

Element Balance for 6434 Gas Phase Operation with Bituminous Coal Middle Oil

	Total Tons	Carbon Tons	Hydrogen Tons	Nitrogen Tons	Sulfur Tons	Oxygen Tons
Middle Oil	1000	865.5	134		0.5	
Fresh Gas 192,000 M^3	23.3	2.4	15.9	4.9		0.1
Total Feed	1023.3	867.9	149.9	4.9	0.5	0.1
Gasoline	565					
Cold Separator Oil		801	136			
Middle Oil	372					
Lean Gas	19.0	7.2	4.9	6.2	0.5	0.2
Rich Gas	63.0	49.4	10.8	1.0	1.6	0.2
NH_3 in Disch H_2O	0.04		0.1	0.03		
H_2S in Disch H_2O	< 0.01					
CO_2 in Disch H_2O	0.02	< 0.01				0.02
Total Outlet	1019.0	857.6	151.7	7.2	2.1	0.4
Balance Difference	-4.3	-10.3	+1.8	+2.3	+1.6	+0.3
Balance Difference in % of Feed	-0.42	-1.12	-1.06	+47	+320	+300

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APPENDIX B

CATALYST PREPARATION

Preparation of 5058 Catalyst.

Old catalyst was roasted in air at 800°C. to convert the tungsten to the oxide.

$$WS_2 + 3\tfrac{1}{2}O_2 \rightarrow WO_3 + 2SO_2$$

The tungsten oxide produced by roasting was either treated alone or combined with an impure tungsten oxide called "gelberde" which contained 92 percent WO_3. These oxides were then treated with filtrate from previous catalyst batches. The filtrate was an aqueous solution of ammonium polysulfide and ammonium thiotungstate, and to this added 10 percent make-up ammonia and hydrogen sulfide. After heating to 50°C. and stirring for about 3 hours most of the oxide was converted into ammonium thiotungstate.

$$WO_3 + (NH_4)_2S_x \rightarrow (NH_4)_2WS_4$$

The solution was filtered to remove undissolved material, and the filtrate was heated up to 70°C. Then the ammonium thiotungstate was allowed to slowly crystallize out with continual stirring for 8 hours, during which time the temperature was lowered to 20°C. The slurry was filtered with nitrogen pressure, and the filtrate was recycled to dissolve more tungsten oxide.

The crystals of $(NH_4)_2\ WS_4$ were not washed, but dried in a nitrogen atmosphere at 100°C for about 3 hours. Great care was taken to prevent access of air to the salt on account of oxidation to the oxysulfide which would result in loss of activity.

$$(NH_4)_2\ WS_4 + 3O_2 \longrightarrow (NH_4)_2\ WO_2S_2 + 2SO_2$$

The dry salt was next heated to 400°C in a stream of hydrogen to convert it into tungsten disulfide.

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Preparation of 5058 Catalyst (cont'd.)

$$(NH_4)_2\ WS_4 + H_2 \longrightarrow WS_2 + 2NH_3 + 2H_2S$$

This operation was conducted in a four pass heated kiln with internal screws. The top two passes were heated and had hydrogen introduced to decompose the salt, while the lower two were unheated and used nitrogen for cooling of the tungsten disulfide.

The WS_2 was dry ground so that the average particle size was about 0.5-1 millimeter. Too fine a powder reduced the mechanical strength of the finished pellets. The powder was then pelleted in a regular pellet press to make pills 10 millimeters in diameter by 10 millimeters high. During the operation it was necessary to maintain an inert atmosphere with nitrogen or carbon dioxide around the dies to present oxidation. The pellets were tumbled around in a mill to remove sharp edges and produce smooth uniform cylinders. The finished catalyst was stored under a nitrogen atmosphere until ready for use.

Some of the important data about 5058 catalyst are given in the following table:

Diameter	10 mm
Height	10 mm
Volume	0.785 cm^3
Weight	3.15 grams
Outer surface/pellet	4.7 cm^2
Weight of 1 liter pellets	2600 grams
Pellet surface/ 1 liter of pellets	0.39 M^2
Compression strength	300 kg/cm^2
Compression strength after 1½ years service	270 kg/cm^2

Preparation of 6434 Catalyst.

Fullers earth was activated by treatment with 8-10 percent of 10 percent HF solution by adding the acid slowly and stirring for about 20 minutes. Then sufficient ammonium thiotungstate was dissolved in the mother liquor from which

Preparation of 6434 Catalyst (cont'd.)

it crystallized to give a 10 percent WS_2 content in the finished catalyst. The ammonium thiotungstate was prepared in exactly the same manner as was done for the 5058 catalyst. The mixture was then heated to about 120° C maximum and stirred for about 8 hours until approximately dry.

The mass was then cooled in nitrogen and ground to about 1 to 3 millimeter size before passing through a kiln at 400°C. similar to that used for the pure tungsten sulfide. A 1 to 1 mixture of hydrogen to hydrogen sulfide was used in the heating process instead of pure hydrogen sulfide and nitrogen. After cooling, about 28-30 percent water was added while stirring to the material to give it good cohesive properties in pelleting. The addition of this water did not make the catalyst mass appear wet, since the Fullers earth absorbed it. The lumpy mass was screened to remove pieces over 3 millimeters, the oversize being reground, and then the power was pelleted in the same manner as was done with 5058.

After pelleting the pills were allowed to dry 3 to 4 hours to improve their hardness, and then tumbelled slightly in the mill. After final drying at 100-120°C, the catalyst was stored in a nitrogen atmosphere until used. Before use an initial heat treatment of 8 - 10 hours in hydrogen at 400-450°C improved the strength.

Some of the important facts about 6434 catalyst are given in the following table:

Diameter	10 mm
Height	10 mm
Volume	0.785 cm^3
Weight	1.24 grams
Outer surface/pellet	4.7 cm^2
Weight 1 liter pellets	800 grams
Pellet surface/liter	0.39 m^2
Compression strength	about 200 kg/cm^2

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Preparation of Welheim Gas Phase Catalyst No. K536.

Approximately 90 kilos of crude kieselguhr paste having a water content of 60 percent were mixed carefully for 30 minutes with 4 kilos of 70-72 percent hydrofluoric acid solution. Then 10 kilos of Fullers earth were added and mixed thoroughly. Next 3.7 kilos of zinc oxide plus 3 kilos of flowers of sulfur were added together with 4.6 kilos 50 percent aqueous solution of chromic acid. After 10 kilos more of Fullers earth had been added and the whole charge thoroughly mixed, it was neutralized with about 9 kilos of 0.916 density ammonia solution. Then 1.4 kilos of ammonium thiomolybdate dissolved in 7 kilos of ammonia solution were added together with 4 kilos of Fullers earth and the whole mass thoroughly mixed.

The catalyst was dried to a water content of 30-33 percent and then pelleted into cylinders 10 millimeters in diameter by 10 millimeters high. These pills were dried 3 to 4 days at 75°C before storing. In order to activate the catalyst, it was necessary to heat it for 12 hours in hydrogen at 350°C. After activation the catalyst contained 0.7 percent Mo, 2.0 percent Cr, and 4.0 percent Zn as the active metallic consituents.

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APPENDIX C

DRAWINGS

No. C-1 Heat Exchanger, 500 mm. diameter, Assembly
C-2 Gas-Fired Preheater, Section
C-3 Gas-Fired Preheater, Thermocouple Location.
C-4 Sump Phase Converter, 1000 mm diameter, Assembly
C-5 Hot Separator, 800 mm. diameter, Top & Bottom Cooling, Assembly
C-6 Hot Separator, 300 mm. diameter, Gas Injection, Assembly
C-7 Cold Separator, 1000 mm. diameter, Assembly
C-8 Expansion Valve, Assembly and Parts.
C-9 Electric Preheater, Assembly
C-10 Gas Phase Converter, 800 mm. diameter, Assembly.
C-11 Gas Phase Converter, 1000 mm. diameter, Assembly.
C-12 Coking Oven, Screw type, Section and Flowsheet.
C-13 Coking Oven, Ball Type, Flowsheet.
C-14 T.T.H. Converter, 1000 mm. diameter, Assembly.

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APPENDIX D

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16. Heizöl- Grossversuch, Ludwigshafen, 1941.
17. Das Ergebnis des Grossversuches K 804 Hinsichtlich der Breiregeneration, Ludwigshafen, 1941.
18. Vorlaufiger Bericht über den Ausbaubefund der Hochdruck Kammer nach der Hiezöl Grossversuch, Ludwigshafen, 1941.
19. Zur Frage 300 oder 700 atu fur Obershclesien, Ludwigshafen, 1941.
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34. Über Hochdruckstähle, 1944.
35. Ergebnis Bericht über Untersuchungen an N10, Leuna, 1943.
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39. Bericht zum Besuch der Leuna Werke (Hydrieranlagen) von 12 August bis 3 September, 1937.
40. Fortschritte auf dem Gebiete der Messung, Regelung und selbsttätigen Betriebsüberwachung von Hockdruckanlagen, Ludwigshafen, 1942.

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44. Selbsttätige Regulung der Sumpf-und Gasphasekammern in der Hydrierung der Leunawerkes, 1944.

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No. 15.

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

Unclassified by
OP-23-F2
Serial no. 4000P23
dated 26 Nov. 1945

80670

TECHNICAL REPORT No. 234-45

USE OF GRAPHITE OXIDE AS A FUEL OR FUEL ASSITIVE

August 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office
New York, N.Y.

File: A9-16(3)(10/Hn)

80671

Serial: 816

22 August 1945.

[redacted]

From: Chief, U.S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U.S. Naval Technical Mission in Europe Technical Report No. 234-45, Use of Graphite Oxide as a Fuel or Fuel Additive - Forwarding of.

Enclosure: (A) (HW) Six (6) complete copies of subject report Nos. 1 - 6, as listed in distribution.

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Captain, U.S.N.,
Acting.

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80672

TECHNICAL REPORT No. 234-45

USE OF GRAPHITE OXIDE AS A FUEL OR FUEL ADDITIVE

SUMMARY

An investigation conducted in Germany in April-May 1945 concerning the use of graphite oxide, as well as finely divided carbon, as a fuel for boiler firing or for internal combustion engines. The result was negative in that it was found that no practical use was ever made of either product.

August 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

80673

[redacted]

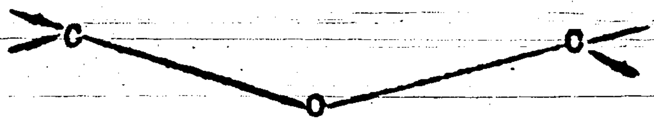
USE OF GRAPHITE OXIDE AS A FUEL OR FUEL ADDITIVE

1. Some rumors having been heard about the use of very finely pulverized graphite, or graphite oxide, prepared by Schering Kalbaum in Berlin, as a fuel or as an additive to fuel, the matter was investigated.

2. In Hamburg, Prof. Zerbe of Rhenania Ossag (Shell) is familiar with the question and reports that this is a process similar to the "Collodial Fuel" about which much is known in the United Kingdom and the United States of America. In other words, finely divided coal carried in suspension in fuel oil for burning in combustion chambers under boilers, etc. Economically it appears no sounder in Germany than in the U. S. A.

3. Not satisfied with this rather meager information, the writer kept on questioning other parties during his two latest missions in Germany about the use of solid pulverized coal, carbon, graphite, etc. either in suspension in fuel oil or for internal combustion engines.

4. It was found that Schering Kalbaum in Berlin had acquired from a Professor Hoffman a license to make "graphite oxide" of formula:



by treating graphite with $KClO_3$ in presence of concentrated sulfuric and nitric acid, also with $K_2Cr_2O_7$ or KMnO4 with concentrated H_2SO_4. Such products have C:O value of 2.5 to 3.5 and heat breaks them up, liberating oxygen.

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Use of Graphite Oxide as a Fuel or Fuel Additive. (Cont'd)

5. The conclusion is that while certain specialists are still toying with the original idea of Dr. R. Diesel of making a pulverized coal internal combustion engine, the matter was dropped (in 1944 only) as unsound and uneconomical. Studies were made, among others, by Dr. Ponsig, of I.G. Farben, at Ungstein near Bad-Durkheim; he expected his company to give him an engine to work on and apparently one was ordered from the Erste Brunner Maschinen Fabrik at Brunnen (Czecheslavakia) where a Prof. Jelizcka was working along the same line, but it was never delivered.

6. It can safely be stated that the matter was dropped well before the end of the war.

Prepared by:

R. J. BENDER
Lieut. USNR

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U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

Unclassified by
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Serial no. 327P23
dated 22 October 1945

TECHNICAL REPORT No. 235-45

8C675

THE PREPARATION OF TETRAHYDROFURAN POLYMERS AS A SYNTHETIC LUBRICANT FOR METALS

August 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

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80676

TECHNICAL REPORT No. 235-45

THE PREPARATION OF TETRAHYDROFURAN POLYMERS AS A SYNTHETIC LUBRICANT FOR METALS

Note: This information forwarded previously as NavTecMisEu Confidential LETTER REPORT 123-45 (s) under same title, file No. Ag-8(10/Ma) dated 12 June 1945, Serial 0310.

August 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

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U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office
New York, N.Y.

80677

File: A9-16(3)(10/hn)

Serial: 0934

27 August 1945.

[redacted]

From: Chief, U.S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U.S. Naval Technical Mission in Europe Technical Report No. 235-45, The Preparation of Tetrahydrofuran Polymers as a Synthetic Lubricant for Metals - Forwarding of.

Enclosure: (A) (HW) Complete copies Nos. 1 - 19 of subject report as listed in distribution.

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2. CNO (OP-16-PT) is requested to forward complete additional copies of this report to such other agencies as may be interested.

Harry D. Hoffman
HARRY D. HOFFMAN,
Captain, U.S.N.,
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[redacted]

SUMMARY

The information given here was obtained from Dr. Delfts of the I. G. Farbenindustrie during an interview at the Leverkusen Plant on May 26, 1945. It has been found that, by a complicated procedure, tetrahydrofuran will polymerize, in the presence of a catalyst, to compounds having properties desirable in a lubricant. Among these are a high flash point, a high viscosity index and extremely low pour point. The nature of the polymeric complex can be changed by the addition of co-polymerizing substances such as ethylene oxide and its derivations. The nature of the polymer ranges from liquid to a relatively tough solid melting about 60 degrees Centigrade. The physical state for a particular use depends upon the catalyst used, the temperature of operation and the molecule ratio of tetrahydrofuran to other co-polymerizing componenets. From a long research it has been shown that the best catalyst is a complex of ferric chloride and thionyl chloride. Special materials of construction are needed because of the corrosive nature of the reaction medium. A simple polymer of tetrahydrofuran has been made which is identical with polybutylene glycol. This glycol and its esters have also been used as lubricants. Compounds have been made for crankcase lubrication of internal combustion engines and for high temperature steam lubrication applications by the co-reaction of tetrahydrofuran with 50 parts by weight of ethylene oxide and 25 parts by weight of ethylene oxide respectively. The involved process of manufacture, the limited availability of the necessary raw materials and the cost would preclude any large scale production of these lubricants in competition with refined natural hydrocarbons.

The production in Germany is illustrated in the following figures:

		1942	1943
Crankcase lubricant	(M620)	7.0 Tons	10.7 Tons
High temperature steam lubricant	(M586)	2.4 Tons	5.4 Tons

No operating or performance data are available for these synthetic oils. The basis for their lubricating value to date is dependent on their physical properties. A synthesis is also described for the production of the tetrahydrofuran monomer from formaldehyde and acetylene by liquid phase condensation.

Enclosed with the original copy of Letter Report 123-45, Reference L, are short reports. Reference A to K, covering in detail the theoretical

[redacted]

Summary (Cont'd.)

chemistry involved in the synthesis and the detailed production procedure. It is suggested that reference be made to these if such information is wanted.

References:

(a) Scientific Paper "Polymerization of Tetrahydrofuran; No. 38; Dr. Morschel; 1 October 1940.
(b) Scientific Report "Polymerization of Tetrahydrofuran" Dr. Delfts, Leverkusen, 13 October 1941.
(c) Scientific Paper "Polymerization of Tetrahydrofuran"; No. 165; Dr. Morschel, 17 July 1942.
(d) "Esters of Polymeric Butylene glycol", No. 208; Dr. Schulte, Leverkusen, 2 September 1943.
(e) Scientific Paper "Esterified Tetrahydrofuran Polymers"; No. 213; Dr. Morschel, 20 September 1943.
(f) Scientific Paper "Brake Fluids"; No. 185; Dr. Morschel, 12 January 1943.
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(i) "Polymerization of Tetrahydrofuran"; No. 227; Dr. Morschel, 31 December 1943.
(j) "Preparation of Polymeric glycols"; No. 232; Dr. Schulte, 10 January 1944.
(k) Four (4) Laboratory Data Sheets - Physical Properties of Tetrahydrofuran Polymer, Exp. No. 2555, 3241, 3484, 5202.
(l) Letter Report No. 123-45(S)

80681

[redacted]

THE PREPARATION OF TETRAHYDROFURAN POLYMERS AS A SYNTHETIC LUBRICANT FOR METALS

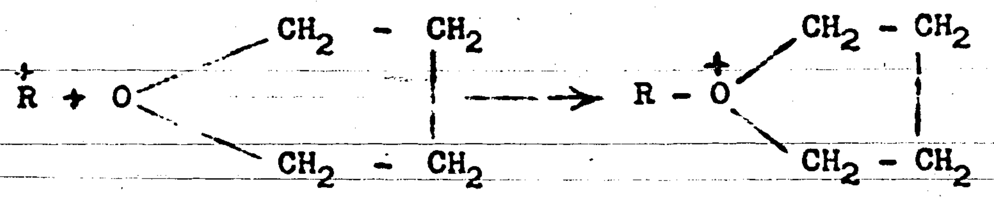
During a research which apparently covered about four years, a series of catalysts, as follows, was developed for the polymerization of tetrahydrofuran:

(1) Tertiaryoxionium salts of acid boron fluoride compounds.
(2) Boron trifluoride - ethylene oxide complex.
(3) Antimony pentachloride.
(4) Aluminum trichloride.
(5) Ferric chloride and thionyl chloride.
(6) Stannic chloride.
(7) Perchloric acid.
(8) Chlorsulfonic acid.

Subsequent work has demonstrated that the best of these, for large scale production, is the ferric chloride-thionyl chloride complex. The basis for this choice is:

(1) Safety in operation.
(2) Ability to give a high degree of polymerization.
(3) Ease of hydrolysis of the terminal groups.
(4) Speed of reaction.

Tetrahydrofuran polymerizes by a free radical or ionic chain mechanism as follows:



(I)

An opening of the furan ring follows with the production of an alkyl-cation.

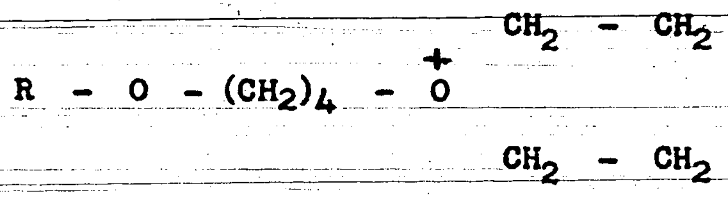
$$\left[R - O - CH_2 - CH_2 - CH_2 - \overset{+}{CH_2} \right] \quad \text{(II)}$$

⑥

[redacted]

The preparation of Tetrahydrofuran Polymers as a Synthetic Lubricant for Metals. (Cont'd.)

The assumption for further reaction is that the ionic state is maintained and that the complex Ion (II) is a reaction initiator capable of further reaction with tetrahydrofuran to give:



$$R - O - (CH_2)_4 - \overset{+}{O}\begin{matrix} CH_2 - CH_2 \\ \\ CH_2 - CH_2 \end{matrix} \qquad (III)$$

This radical (III) in turn undergoes ring fixation to give:

$$R - O\ (CH_2)_4 - O - (CH_2)_3\ \overset{+}{C}H_2 -$$

By this means a chain mechanism is perpetuated until reaction with an Ion of negative charge meets the propagating Ion and removes it from further reaction.

It follows from the above mechanism that chain length is dependent upon catalyst concentration since the greater the amount of catalyst the greater the number of chain molecules present in any preparation.

The polymers range from liquids at room temperature to crystalline solids with a melting point about 60 degrees Centigrade.

The products are soluble in aromatic hydrocarbons, in chlorinated aliphatic hydrocarbons, and in many ethers, esters and ketones. The solubility decreases with increase in molecular weight as is usually the case with macromolecules.

The consistency of the polymeric products may be roughly grouped as follows:

Up to 16 carbon atoms per molecule - liquid at room temperature.
16 " 25 " " " " - vaselinelike.
25 " 50 " " " " - waxy.
50 "100 " " " " - tough wax to brittle.

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The preparation of Tetrahydrofuran Polymers as a Synthetic Lubricant for Metals (Cont'd.)

These polymers are unstable to oxidation, the attack taking place at the carbon atom adjacent to the ether oxygen. Esters and acids are the products of this oxidation. Apparently this sensitivity to oxygen is so pronounced that atmospheric oxygen is sufficient to cause a breakdown. Stability in operation is achieved by the addition of small amounts 1.0 to 3.0 percent of phenyl B-naphthylamine.

In practice for lubricant production tetrahydrofuran is always copolymerized with ethylene oxide or one of its derivatives such as propylene oxide or epichlorhydrin. These copolymerizing monomers tend to keep the polymeric product liquid over wider temperature differences. The more branched the chain of the oxide additive the broader is the liquid range of the polymer.

These polymers have also been tried in applications other than lubricants. These uses are briefly noted as follows: Products containing 18 to 71 carbon atoms per chain are compatible with Buna S and cause a softening which accelerates sheeting in the processing of this synthetic rubber. Polymers containing less than 30 carbon atoms per molecule give no decrease in the strength of the compound Buna S, above 30 there is a decided lowering in the strength of the rubber. Tetrahydrofuran polymers have also been used as a substitute for wool-fat as an aid in spraying Buna S compositions for certain applications. These same polymers have also been used as substitutes for whale-oil for treating leather and as lubricants for synthetic fibers in spinning operations.

It is essential in this process that all reagents be carefully dried before use. This is mandatory for control of the reaction and for best yields. The presence of water hydrolyzes the catalyst giving rise to acidic components.

A typical preparation is briefly outlined. The catalyst is prepared previous to its utilitization in the process by mixing the following:

12 liters tetrahydrofuran
5 Kg. ferric chloride
3 Kg. thionyl chloride

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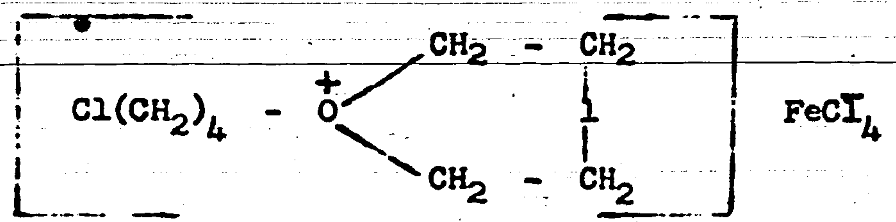
The Preparation of Tetrahydrofuran Polymers as a Synthetic Lubricant for Metals. (Cont'd.)

During reaction of these sulfur dioxide is lost and the product, a crystalline mass is thought to have the following structure:.



This material is isolated and charged back to the reaction so that the concentration of the catalyst based on the total product is as follows:

Component	Engine Lubricant M 620 Molecules	Steam Lubricant M 586 Molecules
Tetrahydrofuran	100	100
Ethylene Oxide	50	25
Thonylchloride	8	3
Ferric Chloride	0.3	0.3

The apparatus used is an iron kettle, equipped with an agitator and open to the atmosphere through a reflux condenser. The kettle is jacketed for cooling. The tetrahydrofuran and ethylene oxide are mixed and fed to the catalyst at such a rate as to maintain a temperature of 28 to 30 degrees Centigrade. Approximately 90 to 95 percent of the tetrahydrofuran enters into the polymer during reaction. The crude oil is washed free of iron salts or corrosion by treatment with aqueous sodium bisulfite, the washed oil is then treated with sodium methylate under reflux to replace the terminal chlorine groups with methoxy groups, then neutralized and stripped of any remaining tetrahydrofuran, water and low boiling compounds by a vacuum distillation.

Typical physical properties of an M 620 oil are as follows:

Solidification point - -27° C.
Flow point - -18° C.

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The Preparation of Tetrahydrofuran Polymers as a Synthetic Lubricant for Metals (Cont'd.)

		Viscosity ° Engler
-20° C.	-	-
0	-	-
20	-	370
50	-	10.2
100	-	2.9
Polhöle (a)	-	1.0

(a) Polhöle is value which corresponds to viscosity index used in American oil industry and has been described in detail in U.S. Naval Technical Mission in Europe Technical Report Number 73, of 6 March 1945.

The tetrahydrofuran used in this lubricant is synthesized by I.G. at Ludwigshafen by a liquid phase reaction described in detail in U.S. Naval Technical Mission in Europe Technical Report No. 105-45 of June 1945.

Prepared by:

F. H. Roberts,
Technician

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TECHNICAL REPORT No. 248-45

THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

September 1945

U·S·NAVAL·TECHNICAL·MISSION·IN·EUROPE

80687

U. S. NAVAL TECHNICAL MISSION IN EUROPE
c/o Fleet Post Office
New York, N.Y.

File: A9-16(3)(10/Hn)

Serial: 1321

6 October 1945

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From: Chief, U.S. Naval Technical Mission in Europe.
To : Chief of Naval Operations (OP-16-PT).

Subject: U.S. Naval Technical Mission in Europe Technical Report No. 248-45, The Synthesis of Hydrocarbons and Chemicals from CO and H_2 - Forwarding of.

Enclosure: (A) (HW) One (1) complete copy of subject report as listed in distribution.

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8C688

TECHNICAL REPORT No. 248-45

THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

SUMMARY

It is the object of this report to describe the commercial application of and the development in Germany, in the Synthesis of Hydrocarbons and chemicals from CO and H_2 during the war.

September 1945

U. S. NAVAL TECHNICAL MISSION IN EUROPE

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SECTION VII (Cont'd.)

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THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2
THE FISCHER-TROPSCH PROCESS

Introduction

The synthesis of hydrocarbons from mixtures of CO and H_2, commonly referred to as the Fischer-Tropsch process, was the object of a coprehensive study by the U.S. Naval Technical Mission in Europe's Petroleum Group in Germany from April through June 1945.

This study disclosed that the process was of secondary importance in the German fuel economy, producing 9.1% of the total German oil supply. The concerted effort of German scientists to improve its two main drawbacks; very low space velocity and poor quality gasoline did not succeed which made it a poor competitor with such processes as coal tar or even coal hydrogenation. It was quite generally agreed in Germany that $CO+H_2$ Syntheses would be used in the future as methods of producing special chemicals and chemical raw materials.

The outstanding quick ignition, ash and sulphur free quality of the diesel oil from FT synthesis would not, in the German point of view, change this picture. No attempts were made to develop engines which could make use of the 90-100 cetane number in a pure FT diesel oil as such. The Germans, being short on all types of hydrocarbons, made good use of the "Cetane" from their FT plants, however, by upgrading diesel fractions from coal tars with cetane numbers of 10-15 and thus increasing their production of 40-50 cetane diesel oil. For this purpose, FT oil was exceptionally suited. The value of cetane number is presently undergoing a re-examination and until this re-examination has been completed, the further use of the Fischer diesel oil is uncertain.

The production of chemicals via synthesis from $CO+H_2$ was still in its early beginnings. The war has slowed down all research not directly connected with the German war effort; but two classes of compounds produced by Fischer-Tropsch synthesis, nevertheless, received particular attention; mono-olefines and high boiling alcohols. These compounds were of great interest, the first for polymerization to synthetic lube oil and for sulfonation to detergents; the second for esterification to special lubricants. The German efforts to increase and control production of these compounds were successful, in that they developed means to enrich these compounds in the primary synthesis products to concentrations of almost 70%.

Introduction (Cont'd.)

The ways used to obtain these yields are described in Sections 1a and 1b.

The FT synthesis is known to be but the sum-total of a great many different reactions, such as carbide formation, polymerization, hydrogenation, cracking, and isomerization. The direction of future research must necessarily be towards better insight into the chemistry of synthesis and the kinetics of the reaction. The Germans have done considerable work along this line and the information obtained from them is reported in Section 1b.

Finally, it is pointed out that only the actual synthesis is considered in this report. Methods to produce the feed ("CO+H_2"), as well as processes based on the primary products are described in the following U.S. NavTecMisEu reports:

(a) The production of H_2 and synthesis gas from Solid and Gaseous Fuels.
(b) The Manufacture and Application of Lubricants in Germany.
(c) The Manufacture of Aviation Gasoline in Germany.
(d) German Diesel Fuels.

SECTION I

THE FISCHER-TROPSCH PROCESS

Contents.

Present Commercial Application.

Contents (Cont'd.)

SECTION I.(a)

THE FISCHER-TROPSCH PROCESS

Present Commercial Application.

1. General Status of Process.

The Fischer-Tropsch Synthesis had reached commercial realization long before the war. It had attracted considerable interest in the United States and finally patent rights were obtained by certain American companies. Late in 1938 a thorough exchange of information took place in Germany followed by an inspection of the plants. Thus all information available at that time may be considered in American hands.

The greatest obstacle to a large scale development of the process was the poor quality of the gasoline it produced. With the beginning of the war only a short distance away, the Germans had to use other means to synthesize high quality fuels, such as high pressure hydrogenation, and in

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1. General Status of Process (Cont'd.)

the same measure as hydrogenation capacity was increased, the expansion of Fischer-Tropsch was brought to a standstill. Thus we find, practically all Fischer-Tropsch plants completed and in operation before the war.

The main sponsor of the process, Ruhrchemie A.G. expended great effort to develop processes to improve the fuel quality of the primary product, but the fact was finally recognised that Fischer-Tropsch using cobalt catalyst primarily could be of value as the means to produce chemicals rather than fuels, with diesel oil a possible exception.

The first objective was the production of olefines and the subsequent conversion of the olefines to such products as synthetic lube oils or high-boiling alcohols. The Germans succeeded in this development.

The next step would be the direct synthesis of more valuable compounds, such as high-boiling alcohols and esters. The work done in this connection is described in Section 2 of this report (Synol).

In the following chapter, information is presented regarding operation, production and cost of product from existing plants.

2. Location and Production of Commercial F-T Plants in Germany.

During the war, Germany suffered from a great shortage of hydrocarbons, and the oil produced via FT represented a substantial part of the total domestic production as can be seen from the following table:

Source of Product	Total Capacity Tons/Year	%
H.P. Hydrogen'n	3,918,000	60.1
FT Synthesis	591,000	9.1
German Crude	1,920,000	29.5
Bituminous Coal Tar	36,000	0.5
Brown Coal Tar	50,000	0.8
@	6,515,000	100.0

@ Data from Dr. Buetefisch, Secretary Oil Section German Industry.

These figures give the installed capacity of the plants. It must be understood that Allied bombing substantially reduced production during the last years.

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2. Location and Production of Commercial FT Plants in Germany (Cont'd.)

The first firm to operate FT plants was Ruhrchemie A.G. who sponsored the development of the process and exercised some control over all other plants through license and catalyst preparation and regeneration. There were only three plants in Germany where catalyst was made, 2 of which were under direct Ruhrchemie control. In the next table is given a list of the F-T plants which operated in Germany (a small unit is operated by the Kuhlmann Co. at Harnes, France, 11,000 T/year).

GERMAN FISCHER-TROPSCH PLANTS

Name of Operator	Location	Capacity Tons/Yr.	%	M tons/month - Avg.Monthly Prod Motor Gasoline	Diesel Fuel	Wax & Kogasin	Lube Oil
Ruhrchemie	Holten, Ruhr	72,000	12.0	2.1	0.8	1.4	1.2
Gewerkschaft "Viktor"	Castrop-Rauxel, Ruhr	40,000	6.8	1.5	1.0	0.8	-
Rheinpreussen L.u. GH.	Moers, Ruhr	70,000	11.8	2.8	2.1	1.1	0.2
Krupp Benzin	Wanne-Eickel, Ruhr	60,000	10.2	2.2	1.1	1.7	-
Hoesch Benzin	Dortmund, Ruhr	47,000	7.9	0.5	1.2	2.0	0.2
Braun Hohle Benzin A.G.	Ruhland, Saxony	170,000	29.2	8.4	2.5	3.1	-
Essener Benzin A.G.	Berghamen, Ruhr	80,000	13.6	4.1	1.8	0.8	-
Schaffpotsch Benzin Gm GH.	Deschowitz, Silesia	40,000	6.8	0.7	0.8	1.8	-
Wintershall A.G.	Luetzkendorf, Saxony	(70,000) 12,000	1.7	0.2	0.1	0.7	-
TOTAL:		591,000	100.0	22.5 (46.1%)	11.4 (23.3%)	13.4 (27.4%)	1.6 (3.2%)

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2. Location and Production of Commercial FT Plants in Germany (Cont'd.)

Of the existing 9 FT plants, 5 were of the low pressure ("Niederdruck") type, 2 included both low pressure and medium pressure, and 2 were of the medium pressure ("Mitteldruck") type. The distribution of these plants and their capacities is shown in this table:

DISTRIBUTION OF LP(1) AND MP(2) CAPACITY AMONG FISCHER-TROPSCH UNITS
(Based on actual production for 1942)

Name of Plant	LP Operation T/Year	MP Operation T/Year	Total T/Year
Ruhrchemie	18,088	44,545	62,633
Viktor	37,699		37,699
Rheinpreussen	67,212		67,212
Krupp *	48,330	11,857	60,187
Hoesch		46,044	46,044
Brabag	164,606		164,605
Essener	79,974		79,974
Schaffgotsch		26,374	26,374
Wintershall	11,468		11,468
TOTAL:	427,377	128,820	556,197
%	76.8%	23.2%	100.00%

* In this plant the first stage operates at low pressure; second stage at medium pressure.

The last FT unit, a medium pressure plant, had been built in 1937 (completed 1939). However, it was found that this product was even less suitable for motor fuel due to its lower olefine content and no further units were built.

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2. Location and Production of Commercial FT Plants in Germany (Cont'd.)

In the meantime, a new type of operation was developed, consisting mainly of gas recirculation ("Kreislauf") which, on MP operation gave substantial increase in the production of olefines. This process is described in detail in this report. Two of the existing MP plants were in the process of conversion to "Kreislauf" but neither had begun to operate and all information is based on pilot plant data. (1) Low Pressure; (2) Medium Press.

To give a more detailed picture of the production and product distribution of the FT plants, the following table has been prepared. This table is based on actual production for the year 1941. (the data was taken from the licensing invoices of RCH(1) to the 9 licenses).

Note that these figures do not agree with those shown on Table II which covers the following year. The difference is due to the addition in plant capacity in that period. By 1943 the decline in production caused by Allied air activity had already begun.

The figure, barrels/day, is only an approximation based on an average density of 7.5 lbs/gal. (See reference 1a at end of this section).

PRODUCT DISTRIBUTION OF FT UNITS FIGURES IN TONS/YEAR (1941)

Name of Plant	Fluessigas (gasol)	Gasoline	Kogasin (230-320°C)	Diesel Oil	Paraffin (Gatsch)	Hard Wax	Other Products not sold directly	TOTAL
Ruhrchemie	8988	20616		8454			14855	52913
Viktor	4471	18167	3358	7395	2927	833	24	37175
Rheinpreussen	7379	34191	6656	16394	5093	1408		71122
Krupp	4657	25531		11467	5575	2500	8645	58375
Hoesch	3591	9523	3749	15287	5788	351	6110	44055
Brabag	8421	77955		31845	9812	3230	8864	140177
Essener	10415	32574	4767	17007	6199	1351		72312
Schaffgotsch	1557	6035	56	5320	4441	1441	1640	20490
Winterschall	5	3388	838	631	503	195		5561
T O T A L :	49484	227980	19424	113800	40388	11309	40138	502175
%	9.81	45.57	3.86	22.50	8.00	2.55	8.00	100.00
Barrels/Day	948	4380	372	2175	755	216	770	9620

(1) Ruhrchemie Holten

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2. Location and Production of Commercial FT Plants in Germany (Cont'd.)

Although German price figures are not a good basis for calculation in other countries, they were used as the basis for calculating license fees to RCH. The prices for different FT products are given below:

Fluessiggas: $C_3 - C_4$	22 - 26.6	Pfennig/Kg.
Gasoline: Stabilized	25.7-31.5	"
Diesel oil	23.0-27.0	"
Paraffin Gatsch	20.5-25.0	"
* Special Waxes	56.0-92.0	"

* This figure depending on melting point.

The total realization for the primary products for 1941 broken down according to plants was as follows:

Ruhrchemie	13,504,550	- RM/year	25.40	Rpfg/Kg.
Viktor	9,788,611	"	26.30	"
Rheinpreussen	20,467,303	"	28.70	"
Krupp	16,987,486	"	19.20	"
Hoesch	12,114,410	"	27.99	"
Brabag	42,141,536	"	30.20	"
Essener	20,677,082	"	28.50	"
Schaffgotsch	5,978,738	"	29.15	"
Wintershall	1,685,762	"	30.31	"
TOTAL:	143,345,478	- RM/year	28.4	Rpfg/Kg.

The license fee to Ruhrchemie A.G. was exactly 1% of the net sales value of the products.

For the year 1941:

Total Production:	502,175	ton/year
Total License Fee	1,433,454	RM/year
License	2.85	RM/ton product.

3. Catalyst.

(1) Supply of Cobalt Catalyst. (See reference I (a)/2 and I (a)/3 at end of this Section).

All existing plants (LP and MP) were operated with the Standard Ruhrchemie Cobalt-Thoria-Magnesia-Kieselguhr catalyst. This catalyst was supplied from 3 catalyst manufacturing plants.

3. Catalyst (1) (Cont'd.)

From the above tables it can be seen that the FT capacity in Germany was located in 3 different regions as follows:

Location	Total Capacity (ton/year)	%
Ruhr	353,749	63.67
Saxony	176,074	31.60
Silesia	26,374	4.73
TOTAL	556,197	100.00

The three catalyst plants were located accordingly:

Name of Company	Location	Capacity (oven fillings/month) *	
Ruhrchemie	Holten	100	50.0
Brabag	Ruhrland	65	32.5
Wintershall	Luetzkendorf	35 **	17.5
TOTAL:		200	100.00%

* One oven filling : 10 M^3 : 0.9 ton cobalt (average)

** Later increased to 85 to make up for bomb damage at Holten.

The overall yearly German cobalt consumption for FT plants was between 85 and 95 tons. The cobalt resources of Germany were barely enough to keep all FT plants operating during the war, particularly with Finland the only supplier of the metal. There was no shortage of Thoria.

In the handling of the catalyst in the synthesis, and during reworking in the catalyst plants losses were incurred. These losses differed substantially between Ruhrchemie and Brabag. This may be due to the size of the plant and the fact that Brabag is a more modern installation.

The figures obtained in actual operation are as follows:

Plant	Loss of cobalt in Synthesis	Loss of Re-working	Total Loss
Ruhrchemie	4.0%	4.0%	8.0%
Brabag	1.0%	1.5%	2.5%

Based on a production of 400 tons primary product per ton cobalt catalyst and using the Brabag figure this would give 16,000 tons of product ultimately produced per ton of cobalt metal.

The production method of the catalyst has not been changed since 1938

3. Catalyst (1) (Cont'd.)

with the exception of a new forming and drying device which is described below.

The impending shortage of cobalt had led to a large scale development program to replace this metal with iron. This work was a continuation of earlier attempts to produce a better fuel over iron catalysts.

Research along this line was carried out by the following companies:

- I.G. Farben (along 4 or 5 different lines)
- Ruhrchemie
- Rheinpreussen
- Brabag
- Lurgi
- Kaiser Wilhelm Institut (Muehlheim)

The detailed result of these efforts is described in Section I.(b). While good catalysts had been developed for a variety of purposes, none was found that could replace cobalt in the existing units.

The operating temperature of iron catalyst is inherently above that of cobalt. Since the reactor cooling systems had been designed for steam pressures corresponding to cobalt operating temperatures, the substitution could not be successfully accomplished despite the claims of some companies.

4. Preparation of Cobalt Catalyst.

The Cobalt Catalyst used today differs only slightly from the one used in 1938 prior to the exchange of information between U.S. and German engineers.

Composition:	Cobalt (Co)	100 pts.
	Magnesia (MgO)	10 pts.
	Thoria (ThO_2)	5 pts.
	Kieselguhr	200 pts.

The same catalyst would also be used in the Kreislauf operation except for a higher Kieselguhr content (dilution).

The preparation of this catalyst up to the forming and drying of the filter cake was identical as in 1938. A new drier had been developed which would at the same time form the catalyst and give a minimum of abrasion loss in handling. The drier consisted of a drum of 2 m. long and 1.5 m. dia.

4. Preparation of Cobalt Catalyst (Cont'd.)

The outside was studded with small toothed rails, which would serve as molds. The filter cake was pressed on to the drum and the identation of the mold filled to give small (3 mm.) cylinders. The drum rotated slowly (0.1 RPM). At the same time hot gases were passed through the cake filled molds drying the catalyst particles before they would reach the bottom position of the drum, where having contracted slightly during drying, they drop out by gravity. Air or superheated steam could be used for drying purposes.

This method of handling the catalyst made it possible to use a Kieselguhr which had been processed at 700°C. and was softer than the material treated at 1000°C. The softer Kieselguhr gave a more active catalyst (apparent density 130-150 gm/100 cc.)

The reduction of the catalyst is carried out with dry CO_2 free gas ($H_2 - N_2$ mixture or H_2 alone). CH_4 is not a detrimental component of the reducing gas. H_2O, CO_2 CO, NO_2 are all undesirable. The presence of CO_2 is detrimental due to the shift-reaction, which is catalyzed, forming small quantities of CO. This CO is further reduced to CH_4 causing local overheating on the new and highly active catalyst.

The effect of CO_2 in the reducing gas is quite pronounced: with 1 gm/m^3 gas, the reduction is 50%. With no CO_2 in the gas, reduction is 60-65%.

While reducing the catalyst, the necessary heat is supplied with the reducing gas. A temperature of 400°C is reached within 3/4 hours and maintained for a very short time to complete the reduction. The CoO; CO; H_2O; H_2 equilibrium at 400°C governs the extent to which the oxide is reduced. Co. 60% - CoO 40% is the correct ratio in a good catalyst. The extent of reduction is determined by measuring the $cm^3 H_2$ evolved from a known weight of catalyst, upon addition of H_2SO_4.

For the production of olefines both RCH and Lurgi proposed to thin out the catalyst with more Kieselguhr, the catalyst otherwise being identical. About 250-300 pts. Kieselguhr would be used instead of 200 pts. for every 100 pts. of cobalt.

5. Production Data from Commercial Large Scale Operation.

(See reference I (a)/5 and I (a)/6 at the end of this Section).

In the following paragraph some commercial operating data from the largest FT plant are given. Since most processing details are known in the

5. Production Data from Commercial Large Scale Operation (Cont'd.)

United States, it was considered more important to report the overall results rather than describe minor operational changes during the war, which revolve around variations of space-velocity, or catalyst life and similar problems.

No basic changes were made in the actual operation of FT plants up to the collapse of Germany. The data posted below were taken from the balance sheet of the Brabag Plant at Ruhland, covering operations in 1943 and 1944. The plant in question is the largest FT unit. It is of the two-stage LP type using standard cobalt catalyst.

For the year 1943 the following figures are given; they are monthly averages based on the entire 12-month period of Jan. 1 to Dec. 31, 1943.

(1) Gas Production.

Total Synthesis gas produced	116,736,300 m^3/month.
$CO+2H_2$ in gas	79%
Yield of gas from brown coal briquets	1.107 m^3/ton

(2) Synthesis.

(a) Production:

Kondensatoel	6306.1 ton/month	52%
Primary Gasoline	5842.0 " "	48%
Liquid products total	12,148.1 ton/month	100%
Pure gasol	2,836.7 " "	23.2%
Total	14,989 ton/month	
Tailgas	42,165,100 m^3/month - 30.1% of gas feed.	

(b) Yields:

Liquid products/ton briquet	127.4 Kg.
Pure Gasol/ " "	29.8 Kg.
Total:	157.2 Kg.
Liquid products/m^3 Gas	104.1 gram
Pure Gasol " / "	24.3 gram
Total:	128.4 gram

(3) Processing of Primary Products.

(a) Production of materials for sale.

Gasoline	6532.3 tons/month
Gasoline in diesel oil	569.7
Diesel oil	1987.6

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5. Production Data from Commercial Large Scale Operation(3)(Cont'd.)

(a) Production of materials for sale(Cont'd.)

Adsorber gasoline bottoms	557.5	tons/month
Adsorber gasoline	703.1	"
Paraffingatsch	1160.5	"
Kogasin II	2085.1	"
Liquified gases	1228.4	"
Wax	454.4	"
TOTAL	15178.6	tons/month
From outside sources	415.8	tons/month
From Synthesis proper	14762.8	"

(b) Yields:

Sales products/tons briquets	154.6 Kg.
Sales products/m^3 Synthesis gas	126.5 gram
Sales products/ton Primary Product	982.0 Kg.

(4) **Financial Statement.**

(a) Balance:

Out of pocket Cost	3,005,000	RM/month	199.21	RM/tons
Overhead and license	187,000	"	12.40	"
* Capital interest	688,000	"	45.61	"
Amortization	1,118,000	"	74.12	"
TOTAL:	4,998,000	RM/month	331.34	RM/tons
Sales:	4,739,000	RM/month	314.17	RM/tons
Loss:	259,000	RM/month	17.17	RM/tons

* Note the capital cost is excessive. This may have been for reasons not connected with operation of the plant.

(b) Cost Breakdown.	RM/month	RM/ton prod.
(1) Material Cost		
Briquets (at RM 9.60/ton)	920,000	60.99
Outside Coke(at RM 34./ton)	304,000	20.15
Grude Coke (at RM 23./ton)	66,000	4.38
Raw coal (boilers)(at RM 2.4/ton)	14,000	.92
Outside power (at Rpfg. 1.9/KWH)	61,000	4.04
Catalysts	145,000	9.61
Purification (charcoal)	18,000	1.20
Licenses	47,000	3.12
TOTAL:	1,575,000	104.41

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5. Production Data from Commercial Large Scale Operation (4)(Cont'd.)

		RM/month	RM/ton prod.
(1)	Material Cost		
	Income from $NaNO_3$ (RM 95./ton) and other chemicals (RM 35./ton)	154,000	10.21
	Net Total Materials Cost	1,421,000	94.20
(2)	Other Costs.		
	Hourly Wages	706,000	46.80
	Salaries	290,000	19.23
	Other costs	635,000	42.10
	Overhead	140,000	9.28
	5% capital interest (basis: 165 million RM)	688,000	45.61
	9% Amortization (basis: 149 million RM)	1,118,000	74.12
	Total Operating Expense:	4,998,000	331.34

It is interesting to compare the operating costs of HP Hydrogenation with FT synthesis. The Brabag, aside from operating the largest FT plant, also owned three (3) HP Hydrogenation units. Some comparative figures for those plants are given here. They are based on the second quarter of 1943.

	FT (Ruhland)	HP Hydrogenation (Boehlen)	
Primary Product	15,201	21,630	tons/month
Total Production Cost	307.67	251.20	RM/ton prod.
Feedstocks			
Browncoal Tar	-	1.223	ton/ton prod.
Browncoal coke	-	0.803	ton/ton prod.
Browncoal briquets	5.791	-	ton/ton prod.
Utilities			
Steam	11,635	3,346	ton/ton prod.
Water	218,219	247,600	m^3/ton prod.
Power	836	1,210	KWH/ton prod.
Investment			
(Interest and Amortization)	732.29	323.79	RM/ton prod.
Production	3.384	5.570	ton/month/employee

The comparison may not be fair on all accounts since these plants were operated under wartime conditions with Ruhland employing about three times as many foreign workers as Boehlen. This fact may be of importance.

6. Operating Conditions.

The main variables of the operation, such as pressure, temperature, space-velocity, gas composition are today practically the same, as in 1937-1938. Specifically, there was no improvement or change in the design of the ovens. Nevertheless there was no increase in the average yield expressed in gram/m^3 feed gas from approximately 100 g to 130 g/m^3. As Germany was faced with a serious lack of cobalt, the yield of product per ton of cobalt was of greatest importance, since this yield can be raised by keeping the space-velocity low, most plants were operated at less than 100 V/H/V (Vol feed gas/hr/unit volume catalyst).

The Essener Steinkohlen A.G. apparently had developed a somewhat improved method of operation, which resulted in a better yield based on feed, and longer catalyst life. This operation widely discussed by the FT group, was known as the "Essener Fahrweise".

In principle, it consisted only in a rigorous control of operation, i.e.;

(1) Absolute constant feedgas rate and composition.
(2) Countercurrent regeneration of all ovens.
(3) Low-space velocity (increased number of ovens).
(4) More equal distribution of load between stages.

With these means the Essener plant obtained the following results:

	Essener	Others
Yield	160	130 C_3+ gm/m^3 gas.
Catalyst life	2000	1400 hours
Catalyst yield	425	250 ton/ton catalyst

Flexibility of Operation. In order to show the variations possible in FT plant operation, yields and product qualities for 2 conditions listed below. The data are based on a report from Brabag and refer to their Ruhland plant:

	Case I	Case II
Processing		
Absorber gasoline	160°C EP	140°C EP
Diesel oil	160-300°C Max.	under 325°C
Gatsch	over 325°C	over 325°C

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6. Operating Conditions (Cont'd.)

	Case I	Case II
Yield.		
Gasol	5100 ton/year	7600 ton/year
Gasoline	73800 "	83900 "
Diesel oil	52500 "	35100 "
Gatsch	10100 "	10100 "
	141,500 ton/year	136,700 ton/year
Products		
Gasoline: sp.gr.	0.686	0.689
Octane No.	56	62
Diesel oil: sp.gr.	0.757	0.732
Pourpoint	- 20°C	- 60°C
Flashpoint	+56°C	+25°C
Vis E/20	1.08	1.022
Cetane No.	100	88

The difference is due to a variation in the amount of thermal cracking of the distillation fraction carried out in a separate unit.

7. Medium Pressure Fischer-Tropsch Units.

(a) General. The medium pressure units were expected to give more higher boiling materials, particularly wax and also to have a longer catalyst life. However, they had the disadvantage of giving a very paraffinic gasoline (still the most important product) with a lower octane number.

In the meantime processes had been developed which used Fischer olefines as feedstock, and it became necessary to revise operations to produce a maximum of olefines. The Germans succeeded in these attempts. The development was carried through by Ruhrchemie, Hoesch, and Lurgi. By the end of 1944 the RCH and Hoesch plants had substantially completed the construction of equipment to produce a maximum of olefines on their MP-FT units.

The process used consisted in a combination of staging and gas recycle ("Kreislauf"), the operating temperature being substantially unchanged. Plants could still use the original reactors and the standard cobalt catalyst as furnished by Ruhrchemie.

(b) Development of 3-stage Operation. The Hoesch MP pilot plant had

8. Kreislauf Operation (Cont'd.)

While the specific output had thus considerably been improved, there was still the low olefine content of the products which had to be overcome. This was finally done by the use of gas recirculation.

It had been found that at higher pressure the cobalt catalyst reduced the CO almost exclusively under formation of H_2O. Thus it is possible to feed a mixture to the reactor, with very high CO: H_2 ratio, without at the same time losing any CO to CO_2. The increase in the ratio does however raise the olefine content of the product. The tailgas of such an oven is obviously very high in CO and low in H_2 and thus affords a means to further increase the CO/H_2 ratio of the feed to this oven by recycling the gas, preferably after removing all products. This is important to prohibit possible hydrogenation.

The operation with Kreislauf is thus simply an extension of the three-stage operation described above. In practice, it was found that any increase in the ratio recycle-gas: feed-gas over 3:1 does not give sufficient further increase in olefines to warrant the expense. The olefine content of the gasoline cut (200°C EP) is around 70%, the Kogasin cut (200°-325°C) is around 45%.

The temperature required to give adequate conversion is somewhat higher than in ordianry cobalt operation but does not exceed 225° C. This can be reached with the existing steam-cooled reactors.

The Kreislauf was considered of great importance and the entire MP section of the RCH plant was to be used as first stage with Kreislauf. The LP Section would be operated with the exit gas from the MP plus the required hydrogen addition to give the 2:1 ratio, which is imperative in LP cobalt plants. In this arrangement 80% of the total plant production would have come from the Kreislauf.

Pilot Plant Data on Kreislauf Operation. At Hoesch a single reactor had been operated at length with gas recirculation and data from two identical ovens, one with, the other without Kreislauf, are given below:

	Kreislauf	Once Through
Space velocity (basis $10m^3$ cat.)	1060 m^3/hr	1015 m^3/hr.
Ideal gas "	861 "	827 "
Catalyst space velocity	1.35 m^3/hr/kg cobalt	1.23m^3/hr/kg cobalt
Contraction	69%	57%
CO Conversion	85%	69.5%

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8. Kreislauf Operation (Pilot Plant Data on Kreislauf Operation)(Cont'd.)

	Kreislauf	Once Through
CO+H_2 Conversion	89.8%	74.3%
Temperature	195° C	189° C
Average daily production(liquid)	2715 kg.	1835 kg.
Yield	131 gm/m^3 ideal gas	98 g/m^3 ideal gas

The test oven was operated 3650 hours. During the first 2764 hours (almost four months) the oven temperature remained unchanged at 195°C, the pressure at 7 atm. The space velocity was 1200 m^3/hr. for 1 month and 1000 m^3/hr. for the rest of the period. Recycle to fresh feed ratio was 2:1 in the beginning and later raised 3:1, but the difference in the result was not large within that range. The oven contained 2660 kg. catalyst with 785 kg. cobalt. The catalyst was the standard cobalt catalyst used throughout the plant.

The advantages derived from this operation are as follows:

(1) The oven may be brought on stream without loss of time usually required for this operation. In about 5 hours the oven is in full production. Synthesis gas is allowed to enter slowly and the recycle blower is started up while at the same time the pressure is allowed to build up. This is done at around 100° C. Next the temperatures is raised and fresh gas is added as the conversion starts in order to keep up the pressure. Finally the exit valve is opened and the unit is on stream.

(2) The yield per cubic meter synthesis gas is increased. Thus in the first stage alone, the same yield may be reached as formerly in two stages.

(3) Higher space velocity. Therefore fewer ovens are required for a given output. The increase is in the ratio of 3:2 if compared with two-stage once-through operation.

(4) Lower catalyst cost. This is apparent from (3).

(5) The unit is less susceptible to operating disturbances of variation in feed gas composition.

(6) Higher olefine concentration in the products.

In general the application of recycle lowers the boiling point of the product towards lighter materials, but this may be corrected by raising the CO:H_2 ratio as described above.

9. Cost of New FT Plants.

(See also reference I(a)/7 at end of this section).

It is interesting to note German figures on the cost of Fischer synthesis plants. The following data was obtained from Lurgi; (Basis 100,000 T/year plant)

Synthesis section and recovery 400 RM/ton year product.
This based on newest Fe catalyst using Kreislauf and Staging.
Complete Unit including Gas generator 900 RM/ton year product.
These costs are high compared with the following figures from I.G. based on Cobalt multiple stage operation without Kreislauf:
Synthesis section and recovery 290 RM/ton, year product
Complete unit including generator basis coke: 590 " " "
Complete unit including conversion basis natural gas: 500 " " "

The I.G. figures are based on 180,000 T/year capacity. When the plant size is reduced to 100,000 ton/year the cost of the complete unit (basis coke) is increased to 615 RM/ton, year product.

10. Products from Fischer - Tropsch Plants.

(See also reference I(a)/12 and I(a)/13 at end of this section).

During the last years the use of primary Fischer products was of course governed by wartime necessity. In general, it may be stated that a peaceful development would probably have led to the eventual disappearance of the FT product from the fuel picture, with the possible exception of the Diesel cut. Yet it was just this fraction that was also the starting material for a number of syntheses. As to the value of the diesel oil, it remains to be seen whether FT oil may have other special properties which are not yet recognized today, which make it highly desirable as a diesel fuel. The cetane number is, of course, known to be high (90-100). In Germany the fuels were used exclusively to blend up certain low cetane stocks like coal tar oil.

The properties of the LP and MP cobalt synthesis are well known and listed below:

(1) "Gasol-Fluessiggas" C_3 and C_4. The olefine content is fairly high as shown on the next page:

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10. Products from Fischer-Tropsch Plants (1)(Cont'd.)

LP gasol contains 50-55% olefines
MP " " 25-30% "

Kreislauf would have produced 80% olefine in this fraction. The ratio of $C_3:C_4$ is approximately 1:1, with the butane cut containing 1-20% isobutane. This gas is used widely in Germany as a motor fuel and is bottled in the plants.

(2) FT Gasoline. In one case (Rheinpreussen) these olefines are used in the manufacture of isopropyl and isobutyl alcohols by sulphuric acid hydration. The bulk of the fraction is used as motor fuel. In many cases it is blended with benzene which is usually available from adjacent coking plants. No FT gasoline is used for aviation purposes.

The following properties are generally given:

	LP	MP
For 150°C EP gasolines:		
Olefine content	33%	19%
Octane No. (Res.)	57	38
For 200°C EP gasolines:		
Octane No. (Res.)	43	25

The product has a straight chain character. It was found that on the average one out of thirty carbon atoms was a tertiary.

Rhurchemie had developed processes to improve the quality of the gasoline. These include catalytic cracking, aromatization, olefine isomerization. These processes are dealt with in U.S. Naval Technical Mission, Eu. report entitled, "The Manufacture of Aviation Gasoline in Germany."

(3) Diesel oil. This fraction commonly called "Kogasin" ranging from 150 to 325°C was used either as fuel or raw material for chemical synthesis.

Diesel fuel was prepared by blending FT product with certain low cetane stocks ([redacted] residueum) to give a 40-45 cetane diesel fuel. According to the season, a lower or higher pourpoint was required. This was obtained by cutting the fractions at various points.

	Summer	Winter
Diesel fuel	150°- 320° C	150°- 250° C
Cloud point	-6° C	-26° C
Pour point	-12° C	-34° C

The FT oil was blended in varying ratios with the taroils according to the required cetane number.

10. Products from Fischer-Tropsch Plants (3)(Cont'd.)

A tar oil oil of 20 cetane, blended with 100 cetane kogasin, required the following percentage of kogasin:

For a 30 cetane blend	10%
For an 83 cetane blend	60%
The diesel fraction contains	10-15% olefines

MP operation gives a slightly better diesel fuel than LP operation

The olefines boiling in the diesel or kogasin range are of great value as charging stock to certain syntheses. The preferred compound is the dolefine (terminal double bond). In general, the $C_9 - C_{11}$ olefines were used for polymerization to synthetic lube oil. The olefine content could be increased by a mild thermal cracking to 60-70% olefines. It was hoped, that the "Kreislauf" operation would produce this concentration in one step.

The $C_{11} - C_{17}$ olefines were used in the oxosynthesis. (See Section 7 of this report.) Here again it was hoped that the Kreislauf would produce fractions sufficiently rich in olefines to be fed directly to the synthesis without previous concentration.

(4) Wax. Waxes are the highest boiling product from FT operations It was for that reason that MP operations became of interest, since they yield somewhat more wax. The wax is obtained as bottom product in the distillation of primary products and by extraction of the catalyst (intermediate regeneration).

The waxes contain practically no olefines. Wax from MP operation has considerably less Isoparaffins compared with LP wax (less than 50% versus 40%). This is an important property, when the wax is to be used for oxidation to fatty acid, since the soaps derived from these acids were found to have superior odor. It is also of importance in the manufacture of lube oil by cracking and Al Cl_3 polymerization, straight chains being preferred. The wax is usually fractionated, with the lower melting part going to cracking (for lube oil synthesis) and the high melting point waxes (100°C) being sold as premium products.

Considerable work was done on the structure of FT waxes. An attempt was made to isolate pure compounds from the hard waxes by fractional crystallization in different solvents. The wax, a product obtained by extraction of spent catalyst from LP operation, was analyzed and the various fractions checked for melting point, molecular weight and other properties.

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10. Products from Fischer-Tropsch Plants (4)(Cont'd.)

The following data were given:

Pour Point	Molecular Weight
63° C	400
84° C	600
96° C	800
106° C	1000

It was found that the synthesis produced all alipathic paraffins from C_1 up to C_{75}. The "Hard Wax" included the range from C_{25} to C_{75}. Indications were that some still longer chains were present. These higher fractions were hard brittle products which could not be scratched with a finger nail.

11. Adsorption of Hydrocarbons on Activated Carbon.

The art of adsorbing the heavier fractions from hydrocarbon gases on activated carbon with subsequent recovery of these fractions by steaming the carbon has been known and practiced for many years. The principal use made of this process by the Germans was the recovery of the so-called "Gasol" (C_3-C_4) fraction from the Fischer-Tropsch synthesis. Adsorption on carbon is peculiarly adapted to this purpose because a large proportion of the reaction product from the low pressure synthesis is not condensable at 20° C, but passes through the condenser with the residue gas. The process operates effectively at low pressure (atmospheric).

A diagram, (reference I(a)/15 at end of this section) showing the method of operating an activated carbon unit fro "Gasol" recovery is included in the appendix. In this scheme the feed gas is Fischer synthesis residue gas from which the gasoline and heavier components have been condensed by water cooling. In operation, at least four adsorbers are required. Each chamber is used successively for adsorption, drying and cooling.

The feed passes from bottom to top through adsorber one, which is in the adsorption stage. There the heavier components are adsorbed on the activated carbon. The lean stripped gas goes to the drying cycle, where it is picked up by blower 5, and heated from 100° to 150°C, in heater 6 along with some circulated dry gas. This gas then passes through adsorber 2, to dry the wet carbon bed which has just been steamed in the desorption stage. The hot wet gas from adsorber 2 , is dewatered in cooler 7, and a large part of the dewatered gas is recycled through blower 5 as shown.

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11. Adsorption of Hydrocarbons on Activated Carbon (Cont'd.)

The remainder, equivalent in volume to the gas from adsorber 1, goes to blower 8, and is further cooled in cooler 9. It then passes through the hot carbon bed of adsorber 3 to cool this bed preparatory to re-entering the adsorption stage. The gas leaving adsorber 3, is partially returned to the cooling cycle while the remainder leaves the system as lean residue gas to be used as fuel or for another synthesis stage.

The circulation is so controlled that when adsorber 1 has reached the limit of its adsorbing capacity, adsorber 2 is dry and adsorber 3 is cool. At this point the valves are automatically changed as follows: Adsorber 1 to desorption, 2 to cooling, 3 to adsorption, and 4 (which has been steamed out) to drying. The series flow of the gas through the three stages serves the additional purpose of picking up any heavy hydrocarbons, that carried through the first adsorber near the end of the adsorption period, in cooling the carbon bed of the third adsorber. This, of course, permits a greater loading of the carbon with the attendant economy of steam.

The desorption is performed with steam, and the gases are driven out of the carbon in the order: CH_4, CO_2, C_2H_6, C_3H_8, and heavier. The three-way valve 12 in the outlet line is open to the inlet of the adsorbing carbon chamber until the CO_2 and CH_4 are driven off in order to recover the small amount of heavy ends that come off. As soon as the C_3 and heavier gases begin to appear, valve 12 is switched so that mixture passes to condenser 13. Here the gasoline and water vapor are condenser by indirect cooling. This condensate is sent to separator 14 where gasol, gasoline, and water fractions are removed. The gasol goes to holder 15. The gasoline goes through after cooler 16 and meter 17 to tank 18. The water condensate is removed from the system.

The gasol from the holder goes through a compression and liquifaction cycle from which the uncondensable portion is recycled to adsorption and the liquid is sent to an intermediate storage tank. The pressure on this tank is maintained by bleeding gas back to holder 15. The gasol and gasoline are both pumped over a cooler and fed together to stabilizer column 19, where stabilized gasoline and merchantable gasol are removed, the rich overhead condensed gas is fed into the stream to the adsorber of the desorption step. At the beginning of the desorption, this gas, since it is quite rich, displaces CO_2 from the carbon bed during the first minutes of desorption, and therefore does not appear in the recycle to the adsorption vessel but goes to condenser 13, thus again saving steam for the

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11. Adsorption of Hydrocarbons on Activated Carbon (Cont'd.)

process by higher loading of the carbon.

The carbon adsorption is sometimes operated as a two stage process. The following operating data were given by the Lurgi Company.

	First Stage	Second Stage
Number of adsorbers	7	4
Diameter of adsorbers, m	5	5.5
Weight of carbon per adsorber, kg.	15,000	18,500
Inlet gas, m^3/hr.	35,000	21,000
C_3 + inlet gas kg/hr.	3,400	1,500
Recovery		
C_5, %	100	100
C_4, %	60	100
C_3, %	10	80-85
Steam consumption, Kg/Kg. Recovered material	2.5-3.0	6.0-6.5
Time cycle, Adsorption, hrs.	1	1/2
Desorption, hrs.	1	1/2
Drying, hrs.	1	1/2
Cooling, hrs.	1	1/2

In the above cases, the carbon used was known as "Supersorbon". It was made from peat and activated by a $ZnCl_2$ - steam treatment. The size of the carbon was 10%, 2.0-3.3 mm. and 90%, 3.3-4.0 mm. A carbon charge will remove about 1000 kg. of gasoline and gasol per kilogram of carbon before reactivation became necessary. It can be reactivated with steam at 800°C in a rotary kiln.

The Lurgi Company has developed a new carbon known as "SK" which is activated with K_2S, and is said to have about twice the capacity for low boiling hydrocarbons as "Supersorbon". The entire output of this carbon was used for gas masks during the war. Its absorption power for benzol from air as compared to that of the "Supersorbon" is presented below:

Concentration of Benzol grams/m^3 air at 20° C	Adsorption in grams C_6H_6/100 g C "Supersorbon"	"SK"
298	49	58
32	40	51
3.2	22	43
0.32	15	31

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11. Adsorption of Hydrocarbons on Activated Carbon (Cont'd.)

A reprint of an article by Drs. Herbert and Ruepping entitled "Benzin und Gasolgewinnung mit Aktivkohle aus den Restgasen der Benzinsynthese nach Fischer-Tropsch, Ruhrchemie"; is included in the appendix of this report. This German article gives data on the recovery of hydrocarbon from Fischer-Tropsch residue gas, including the composition of the desorbed gases from minute to minute.

(See also reference I(a)/14 at end of this section).

SECTION I. (a)

12. List of References.

THE FISCHER-TROPSCH PROCESS PRESENT COMMERCIAL APPLICATION

The German documents listed below are available in the library of the Bureau of Ships at Washington, D.C.:

1. Lizenzabrechnung 1943 - 2 May 1944 Ruhrchemie A.G. letter incl. nine sets of licensing invoices.
2. "Iroerterung d. Kobaltlage", 8 January 1943.
3. "Kobaltkontakt fuer Fischer Anlagen", 19 April 1943, Note from Dr. Gloth to Dr. Altpeter,
4. "Fischer Synthesis Anlage Courrieres Kuhlmann", I.G. Report 3 December 1940.
5. "Betriebsergebnis April-Juni 1943" Operating sheet and Statement. Brabag (Schwarzheide, Boehlen, Magdeburg, Leitz).
6. "Kosten Vorbericht - Schwarzheide" March 1944 - Brabag statement.
7. "Fischersynthese" 100,00 jato: cost estimate, 11 January 1944.
8. "Bericht (No. 317) uber die Kohlewasserstoffsynthese Versuche", Leuna, February 1939.
9. 1 Process flowchart: Krupp A.G. Wanne Eickel.
10. 1 Process flowchart: Lurgi "Kreislauf" Process.
11. 1 Flowchart for Hoesch "Kreislauf" plant, Lurgi drwg. ODS/592
12. Dipl Arbeit W. Beier (Rheinpreussen) 1938 "Erstarrungsverlauf von Paraffingemisch".
13. "Bestimmung des Isoparaffingehalts", I.G. Ludwigshafen by Dr. Leithe, May 1939.
14. "Benzin-und Gasolgewinnung mit Aktivkohle", by Herbert u. Rueping, Lurgi Company.
15. 1 Lurgi Drwg. OAK/121836 charcoal plant flowsheet.

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SECTION I. (b)

GENERAL INTRODUCTION

Development Work - The Fischer-Tropsch Process.

The research carried out in Germany connected with FT operations was directed along the following lines:

Objective	Means Used to Reach Objectives	Name of Organizations Connected with Work
Replacement of Cobalt catalyst in existing plants	Development of Fe catalysts	KWI, Lurgi, RCH, Rheinpreussen, I.G., Brabag
Production of Olefines and wax	Fe catalysts in general	Same as above.
Production of alcohols	Fe catalysts ("Synol" Process)	I.G. (Leuna)
Improved design	Liquid phase Synthesis	Rheinpreussen, RCH, I.G.

This list does of course not claim to be all inclusive but gives the four subjects which appeared to be of greatest interest. It should be understood that item 1, is simply a wartime necessity. While Fe catalysts are generally considered superior to cobalt for a variety of reasons, they do not lend themselves for use in existing LP reactors. The work done on item 1, may be considered as supplementary to item 2.

(1) Fe Catalysts - General. Historically, Fe catalysts are older than cobalt. The first synthesis was carried out in 1922 over Fe catalysts. These tests were conducted at high pressures (100 atm.) and temperatures (400°C). The results were exclusively oxygenated compounds. With decreasing pressure the oxygenated fractions of the products decreased until at around 7 atm., the yield was almost exclusively hydrocarbons.

The decrease in pressure resulted in a corresponding drop in reaction velocity. It was therefore necessary to develop more active catalysts. At the temperatures employed at the time (400° C) these active catalysts had a short life and for this and thermodynamic reasons the temperature had to be lowered further (from 400°C to 200°C) which in turn required still more active catalysts. Cobalt was found to fulfill the requirement and iron was temporarily shelved.

Nevertheless, work on iron catalyst was continued because the lower cost and higher production of olefines were were obvious advantages. The main difficulty was the low activity forcing the operation into a temperature range where CO decomposition (carbon deposit) may occur and where the lighter members of the paraffin homologues are more likely to be found. (This conversion at higher temperature under otherwise equal conditions yields more methan and gasol.)

Before going into some of the details of the German development of iron catalysts it seems appropriate to consider the effect which the elevation of the temperature range has on the equilibrium of the FT reaction. (See reference I(b)1 and 1(b)2 at end of this section). At first it can be shown that lighter products may be expected at higher temperature, other conditions being equal.

The following table gives values of the equilibrium constant "K" for the Fischer-Tropsch reaction for different temperatures and different members of the hydrocarbon series.

The values were calculated by P. Dolch, for the equation:

$$CO + \left(2 + \frac{1}{n}\right) H_2 \longrightarrow \frac{1}{n} \cdot CnH_{2n+2} + H_2O$$

$$K = \frac{(CnH_{2n+2})^{\frac{1}{n}} \quad (H_2O)}{(CO) \quad (H_2)^{\left(2+\frac{1}{n}\right)}}$$

Compound	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_6H_{14}	C_8H_{18}
Temperature						
100° C	-17.69	-13.56	-12.17	-11.67	-10.77	-10.44
200° C	-11.32	- 7.93	- 6.85	- 5.53	- 5.35	- 5.49
300° C	- 7.15	- 4.27	- 3.38	- 3.18	- 2.50	- 2.26
400° C	- 4.23	- 1.70	- 0.94	- 0.83	- 0.19	+ -0.0

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(1) Fe Catalysts - General (Cont'd.)

Note: That the equilibrium is favored by lower temperature and that the lower boiling hydrocarbons are more likely to be formed at higher temperature.

Another fact which should not be overlooked, is the effect of feed gas composition on the equilibrium. This effect is much greater at the higher temperature and may afford a means to direct the synthesis more efficiently.

The data below are shown to indicate the effect of temperature on the susceptibility to changes in feed gas competition. The figures are % yield, based on CO fed for the reaction with n=8 (Octane) at equilibrium, 1 atm. and 349° C.

Feed gas:	Equivalent 1:2 ($CO:H_2$) "ideal"	68.3%
	13.8% N2 Inert	62.9
	Steam: ½ part/1 part CO	54.7
	Steam: 1 part/1 part CO	41.6
	* Excess hydrogen: 5.9%	71.0
	* Excess Carbon monoxide: 17-7%	57.7%

* (Over the ratio 1:2 $CO:H_2$)

On the other hand the corresponding figures for 180° C and butane as the product vary only between 99.42 and 99.69%. The results of the operation depend on many other conditions besides the equilibrium, as shown above, but the effect of temperature in this connection is quite evident.

The following sections report in condensed form the work done by German research on the development of iron catalysts.

(2) Lurgi Gesellschaft fuer Waermetechnik. Lurgi had developed an iron catalyst which was supposed to yield a better (more olefinic) gasoline and would be more rugged than the cobalt type. They also had developed a catalyst, which would be used in a once-through operation, for use in city gas plants to convert the CO in the coke oven gas to CH_4 and hydrocarbons. This would detoxify the gas and at the same time enhance its heating value.

There actually was a unit of this type in construction (city gas plant at Leipzig). It was however of the cobalt type since the gas net of that city was operated at LP. The $CO+H_2$ content of the feed gas was low and thus a very active catalyst was required but as complete conversion is not of great importance, a space velocity of approximately 200 at 250°-270° C was used.

(2) Lurgi Gesellschaft fuer Waermetechnik. (Cont'd.)

For operation with their HP gas producer, Lurgi had used an iron detoxification (CO conversion) catalyst of the following compositions:

Fe	100 pts.	Al_2O_3	9 pts.
Cu	10 pts.	Kieselguhr	120 pts.

Lurgi proposed to use 2 types of iron catalysts. One was precipitated on silica and operated at low temperatures (230° C). This catalyst was designed to give a maximum of high boiling product through polymerization. Its composition was as follows:

Fe	100 pts.
Cu	25 pts.
Al	9 pts.
SiO_2	20-30 pts.

This catalyst is quite active as a cracking catalyst and hence must be run at low temperature.

A condensed flow chart giving process data is attached to this report Lurgi drwg: DS am 103.

The second Fe catalyst was proposed for the production of the maximum amount of gasoline and olefines. The operation required for this catalyst is practically the same, except for the substantially higher temperature. The catalyst is very cheap, being made from Lauta-Masse, a product obtained in the manufacture of aluminum from bauxite. The Lauta-Masse is soaked with $CuNO_3$, the copper is then precipitated with K_2CO_3 on the carrier and reduced in the conventional manner.

The operations proposed for wax production and for olefine production are compared in the table below: (See also reference I(c)5 at end of this section).

Basis: 1000 m^3/hr. fresh feed gas/ 10 m^3 catalyst volume:

	Wax Plant	Gasoline Plant
Catalyst	Precipitated (Fe, Cu, Al)	Lauta-Masse (Cu impregnated)
Pressure	20 atm.	20 atm.
Temperature	230° C	275° C
Processing	2-stage "Kreislauf" in 1st stage only	1-stage with "Kreislauf"
"Kreislauf" gas volume	2500 m^3/hr.	3000 m^3/hr.
Tailgas	480 "	505 "

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(2) Lurgi Cesellschaft fuer Waermetechnik (Cont'd)

	Fresh Feed	Total Feed (1 stage)	Tailgas	Fresh Feed	Total Feed	Tailgas
CO_2	5.8	22.9	28.2	2.8	31.5	48.0
Cn Hm	-	1.4	1.9	-	1.3	2.2
CO	37.6	26.9	22.6	53.2	29.8	16.7
H_2	48.1	31.8	17.0	35.6	19.8	11.3
CH_4	0.1	2.0	2.7	0.1	3.5	5.3
N_2	8.4	15.0	17.6	8.3	14.0	16.5

Yield/m^3 ideal gas:		
FT liquid	146 gm	98 gm
Gasol	15 gm	32 gm
Alcohols	9 gm	5 gm
	170 gm	135 gm

Product distribution:		
Gasoline 200° EP	20%	71%
Kogasin 200-320° C	20%	20%
Soft wax - 320° C	15%	9%
Hard wax - 460° C	45%	
Total Liquid	100%	100%

Olefine Content:		
Gasoline	60%	75%
Kogasin	45%	60%

These data are based on pilot plant runs and may be considered somewhat optimistic. Note that "Kreislauf" is employed in similar manner as for the MP cobalt operation. Since the catalyst consumes CO-H_2 in the overall ratio of watergas; no intermediate H_2 addition is required.

Note: That while over cobalt the recycle actually increases CO: H_2 ratio it does not increase the CO_2 content, since little CO_2 is formed over cobalt. In the case of iron however, the use of recycle implies a very high concentration of CO_2 in the feed of the first stage. Hence the shift reaction is impeded and the CO_2 formation is accordingly suppressed.

It is not proposed to regenerate the Fe catalysts. Their life is expected to equal or exceed that of cobalt. The Fe catalysts, according to Lurgi, are just as sensitive to sulphur poisoning as cobalt. Once 3%S (wt. on Cat.) is absorbed, the catalyst has lost its activity. For a four month life the feed gas should not exceed 0.3 gms/100 m^3. Gum forming constituents in the synthesis gas, a frequent cause of trouble in FT units, are of course the same danger on Fe as on Co.

Oxygen up to 0.2% vol. in feed can be tolerated (possibly more; Lurgi have no data on this).

Nitrogen is considered a poison, as well as NH_3, which should be removed.

(3) K.W.I. (Kaiser Wilhelm Institut, Muelheim) (See reference I(b)/6 and I(b)/7 at end of section). KWI developed a precipitated Fe catalyst using no carrier. The Fe is precipitated as hydroxide from its nitrate solution, washed, filtered, and pressed. In some cases it may also be alkalized. (For exact recipe see below).

It was found that reduction with H_2 reduces the Fe_2O_3 to Fe_3O_4, which does not yet catalyze the FT reaction. Treatment with CO however, gives a highly active catalyst, following the formation of the carbide. This process ("Formierung") must be carried out under very definite conditions.

It was found that operation with high CO/H_2 gas at atmospheric pressure damaged the catalyst. While at higher pressure no such effect could be established. From this it was concluded that the overcarbidization ("Uebercarbidierung") at low pressure was due to the low H_2-partial pressure resulting in a lowering of this hydrogenating activity of Fe.

It was also found that the pressure at which the formation of the carbide takes place has an appreciable effect on the life and sustained activity of the catalyst in subsequent MP synthesis. Influence of pressure during formation on subsequent activity is shown below:

Pressure during Carbidization	Contraction of Synthesis.
9.0 at press.	5%
3.0 "	12%
1.0 "	28%
0.1 "	30%

Thus a low pressure appears essential for the formation of an active carbide which will retain its activity for many months.

(3) K.W.I. (Kaiser Wilhelm Institut, Muelheim)(Cont'd.)

It was also found that for this formation of an active catalyst an optimum temperature exists (other conditions being equal) near 315° C. With lower temperature the activity is definitely inferior, and with higher temperature only a fair activity results.

Extent of "Forming." Aside from temperature and pressure, the space velocity and duration of the forming are also important. Since the reduction and carbide formation, result in the formation of CO_2 this affords a means to control the forming of the catalyst. The latter is considered terminated when CO_2 in the exitgas has passed through a maximum and reached a constant value. Further production of CO_2 then corresponds to deposition of free carbon.

The importance of this forming can be seen from the variation of the subsequent synthesis temperature required for maximum contraction. An Fe catalyst which was put into operation at 15 atm. without "preforming" required initially 290° C for a 45% contraction. At the end of the 5th month this temperature had to be raised to 300° C. A similar catalyst, "formed" 24 hours with CO at 1/10 atms. and 255° C, was started at 250° C and at the end of the 16th month gave a contraction of 50% at 260° C.

Summarizing the "Forming" it consists in treatment of the catalyst at pressures below and temperatures above those used in the subsequent synthesis. It is preferred to "form" with pure CO at high space velocity. During this treatment a certain equilibrium is established between the solid phase and the gas phase. The lower the CO_2 content of the gas used in formation, the better the reduction and carbide formation.

Some work was done on the analysis of these Fe catalysts. In particular magnetic measurements are used to determine the extent of the conversion from Fe_2O_3 to Fe_3O_4 to Fe_3C. Two Curie points are involved in these changes which allow a determination of the conversion by comparison with known mixtures using a calibrated apparatus. There are probably many carbides present in the catalyst which make an exact determination of Fe_3C difficult. Furthermore it is probably the loosely bound carbon in the higher carbides which accounts for the activity of the catalyst. However, KWI found their method of determining Fe_3C a good way of predicting the activity of a catalyst. There seems to be about 70-80% Fe_3C in a good, well formed catalyst after prolonged use. After an initial complete carbidization the Fe_3C content is reduced to this figure and remains constant at this level. The deposition of free carbon on the catalyst is not considered a "poisoning" of the latter, but simply a mechanical disability.

(3) K.W.I. (Kaiser Wilhelm Institut, Muelheim)(Cont'd.)

The Influence of Alkali on the Catalyst. Alkali was found to increase production of higher boiling hydrocarbons as follows:

Alkali	C_3 g/m^3 ideal gas	Wax %	Liquid HC's%	C_{3+4} %
None	140	13	67	20
1/4% K_2CO_3	148	26	56	18
1.0% K_2CO_3	157	42	47	11

The % alkali is wt. % K_2CO_3 based on Fe. metal. High alkali, however, shortens the life of the catalyst.

Addition of Kieselguhr. Contrary to the experience with cobalt, it appears that Kieselguhr is not required for Fe catalysts. The best results were obtained without a carrier.

Treatment with Hydrogen. It has already been pointed out, that the use of H_2 instead of CO for the "forming" of the catalyst gave poor results.

However, intermediate regeneration over the life of the catalyst gives an immediate but short lived increase in activity. The situation is similar to that encountered with cobalt, The regeneration must however be carried out before the contraction has dropped below 45-50%.

Preparation of Catalyst. A hot solution of iron nitrate is precipitated with soda. It was found that a mixture of ferrous and ferric nitrate gave the best result, pure ferric iron was not satisfactory, with pure ferrous an intermediate.

Copper may be added (½% based on Fe) to give a more reproducible result. The precipitate is washed free of alkali, then slurried in a potash solution, fitered, dried and pelleted. Next the catalyst is "formed" in the manner described above and finally purged with CO_2 for transportation. It is also possible to soak it in wax. The particles are thereby covered and can be exposed to air without losing their activity.

The finished carbided catalyst contains 50 g Fe metal in 100 cc Catalyst. The Fe represents about 60% of the total weight.

Products. The chief characteristic is the olefinicity of the product. The C_3-C_4 cut contained around 70-80% olefines; gasoline (200° EP), 50-60% olefines; diesel oil 10-20% olefines. The wax is practically olefine free.

(3) K.W.I. (Kaiser Wilhelm Institut, Muelheim)(Cont'd.)

The olefines and paraffins are mostly normal hydrocarbons. Overall, about 1 carbon atom in 30 is tertiary. Diolefines are absent.

Oxygenated products are characteristic by-products of the Fe synthesis. The yield was given an approximately 13 g/m^3 water soluble products. Aside from alcohols, which are the bulk of the oxygenated products, the usual mixture of acids, esters, aldehydes was found, but it appears that not much work was done by KWI on this phase of the process. The oxygen content of the hydrocarbon phase was given as 0.2 to 2% with most of the oxygenated compounds in the low boiling fractions.

It was found that these Fe catalysts would produce some very high boiling alcohols (with chain length similar to those of waxes) if operated at 50 atm., or higher, but the yields are low and the catalyst has a tendency to form carbonyl at these pressures.

Summarizing the results of KWI work on Fe catalysts it may be stated that a catalyst and a mode of operation was found which gave the following operational results:

Yield: C_3+, single stage	130-160 g/m^3 ideal gas
Catalyst life (without any regeneration)	18 month maximum
Pressure	15 atm.
Temperature	250° C
Space velocity	400 liters gas/Kg Fe (200 VHV)

For best results the feed gas preferably contains an excess of CO over hydrogen but this is not a necessity.

It might be mentioned that Kreislauf operation was not considered favorably here. It was felt that the cost was not justified by the increase in olefines available over a once-through basis.

(4) Rheinpreussen.

The work done by this organization was somewhat similar to that done by KWI. Here too exact studies of the carbide formation were carried out, and a catalyst based on a cheap raw material for use in liquid phase operation was developed.

(4) Rheinpreussen (Cont'd.)

The reason why iron catalysts do not lend themselves to operation at low pressure is explained by Dr. Koebel (Rheinpreussen) as follows:

The Synthesis of hydrocarbons over elements of the 8th Group is based in part on the competing reactions of carbide formation and carbide hydrogenation. It seems that in the case of iron at atmospheric pressure the carbide formation is faster than the hydrogenation. At least a minimum partial pressure of hydrogen is apparently required to hydrogenate the carbides as they are formed and thus keep the active points of the catalyst free for further carbide formation. If the H_2 partial pressure is below the minimum, the catalyst soon becomes "carbided" and loses its activity. This limiting pressure seems to be $H_2 = 0.5$ atm. At one atmosphere starting with water gas and at CO conversion of 60%, the P_{H_2} in the tail-gas is below this figure. At 10 atm. operation, however, under equal conditions, the P_{H_2} in the tail-gas is 3 atm.

It follows that the ability to form carbides does not increase with pressure at the same rate as the ability to hydrogenate. This drawback may, however, be overcome by a treatment of the catalyst, consisting in a formation of carbide at normal pressure, before starting operation at elevated pressure. This procedure was recommended by both Rheinpreussen and the KWI group who had reached the same conclusion independently from each other.

The carbide is formed during the synthesis, if no special "forming" precedes it, but the formation is slow and may not lead to the same carbide since it is formed under different conditions.

Fe_3C is the more desirable catalyst. As the catalyst ages it changes. If the Fe_3C content could be kept up, the activity would remain indefinitely. It may be possible that higher carbides such as Fe_2C are even more desirable but they are difficult to prepare and are unstable.

There is no better means to determine the carbide in a catalyst than magnetic measurements although hydrogenation could be used to determine the "C in Carbide."

Rheinpreussen also studied the effect of alkali on the formation of carbide. Pure Fe_2O_3 was treated with CO to yield carbide, and gave a certain "C in Carbide" value. Upon addition of 1% K_2CO_3, the "C in C" increased by 30% but upon further addition (i.e., 10% K_2CO_3), the "C in C"

(4) Rheinpreussen (Cont'd.)

decreased to 25% below the value of pure alkali free Fe_2O_3. The effect of alkali on catalyst activity is in proportion to these figures.

Copper is frequently added to Fe catalysts. Copper was also found to slightly increase the carbide formation. This is explained by the fact that Cu increases the rate of reduction of Fe_2O_3 to Fe which must precede the carbide formation. This could be interpreted as a confirmation of a statement by Lurgi that copper does not seem to have a catalystic effect in itself but helps in reproducing a catalyst of constant activity. 1% Cu based on Fe is sufficient for this purpose.

Another catalyst was developed by Rheinpreussen using Luxmasse as raw material and adding 0.15-5.0% K_2CO_3 and 0+3.0% copper. A catalyst of this type was kept in operation for 32,264 hours (3½ years). At the end of that period the catalyst supposedly gave 85% conversion at a space velocity of 80 V/H/V and 113 g. liquid product/m^3 ideal gas, plus 32 gm C_3+C_4. These figures were taken from the monthly reports of the Rheinpreussen laboratory but the data presented there were rather incoherent and must therefore be used with care.

(5) Ruhrchemie.

The long experience of RCH with cobalt catalyst operation led them to develop catalysts containing Fe precipitated on a carrier. Their objective shifted from time to time to Fe catalysts for olefine production, for wax production, or for catalysts to replace cobalt in existing FT units. RCH succeeded in developing a good Fe catalyst for wax production which would be operated at exceptionally low temperatures, but the olefine producer did not get beyond laboratory stage.

During the regular FT meeting at Essen in September 1940, Dr. Roelen gave some information regarding the RCH work. Their findings are generally in good agreement with those of other laboratories. The main difference according to RCH of Fe versus Co is the lower hydrogenating capacity of Fe. This results in 3 important advantages.

(a) There is less CH_4 formed despite the fact that all Fe catalysts require higher temperatures than cobalt.
(b) The products are more olefinic.
(c) Fe can consume CO and H_2 over a much wider range.

(6) Ruhrchemie (Cont'd.)

The first advantages allow a variation of operating conditions over a much wider range than cobalt with corresponding varying boiling ranges of the product, without lowering conversion or increasing methane.

The second is obvious as olefines are a very desirable product (for lube oils and Oxo-synthesis).

The third allows the use of straight watergas without shift.

RCH claim, they can start an Fe catalyst by different methods, such as H_2 reduction, watergas reduction or CO reduction. But it appears that here too the "forming" of the catalyst, the formation of the carbide must precede the actual synthesis.

In accord with KWI, it was found that addition of alkali (in very small concentrations) had a decided effect on the boiling range of the product. The following data were given:

Basis: atm. watergas, 245° C.

Alkali content	Gasoline	Kogasin	Softwax	Hardwax
Fraction	-200° C	200-320°C	320-460°C	460° C
0.0- 0.25% KOH	58.5%	24%	14%	3.5%
3% KOH	20.5%	13%	16.5%	50%

While it is possible to vary the results with small changes in catalyst composition without any change in the operation, it is also possible to vary the operating conditions using the same catalyst and thus obtain varying results. For example, an increase in pressure raises the boiling range (same as over cobalt), all other conditions being equal:

Pressure	1.0	5	20 atm.
CO conversion	95	70	75%
Yield gm/m³ ideal gas	90	86	120
Gasoline %	57%	30%	22%
Kogasin %	24%	25%	22%
Wax %	19%	45%	56%
Olefine in gasoline	68%	63%	63%
Olefine in Kogasin	41%	49%	46%

For a proposed commercial operation to give maximum wax production, the following data were given by RCH. The catalyst is a ppt'd Fe cat:

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(5) Ruhrchemie (Cont'd.)

Gas	Watergas	38% CO	48% H_2	(1:1.26)
Pressure	15 atm.			
Temperature	230° C			
Contraction	60%			
CO conversion	80%			
CO to CO_2	25.6%			
CO to CH_4	7%			
H_2 conversion	80%			
$CO+H_2$	80%			
Consumption $CO:H_2$	1:1.24%			

Yield g/m^3 Feed gas	1 stage by test	2 stage calculated	Total
C_3+C_4 (Gasol)	10	3	13
Liquid products	135	20	155
	145	23	168

Product distribution:

Gasoline	200° C EP	16% wt	70% olefines
Kogasin	200-320°	20% wt	
Soft wax	320-460°	22% wt	
Hard wax	460°	42% wt	

This described catalyst was to be used for production of wax. If olefines were the main objective of the synthesis, the same catalyst with a higher Kieselguhr content was used. As much as 10 m^3 of the wax catalyst had been prepared in pilot plant operation. The following information was obtained regarding the preparation of this catalyst:

The iron is dissolved to give a solution of Fe $(NO_3)_2$ (non-ferric Ion), Cu is added as well as Ca $(NO_3)_2$ with Fe: Cu: Ca in the proportions 100 - 15 - 5. The metallic nitrates are precipitated as carbonates by pouring the hot solution into a solution of hot soda. The endpoint of the recipitation is at 6.6—6.8 pH. At the end of the precipitation Kieselguhr is added and the batch is filtered. The cake is washed free of NO_3 (0.4%, Na NO_3 on 100% Fe is maximum), is then slurried in a 20g/lit. KOH solution and again filtered, dried and formed.

The catalyst is next reduced with a mixture of $H_2:N_2 = 3:1$ using a space velocity of 3000 V/H/V in an analogous manner to cobalt catalyst.

(5) Ruhrchemie (Cont'd.)

The reduction is carried out with hot gas (300° C). As soon as the catalyst has reached this temperature the reduction is complete (3/4 hour).

The reduction occurs in steps from $Fe(OH)_3$ ——— Fe_2O_3 ——— Fe_3O_4 ——— FeO ——— Fe. With the stages overlapping, the several oxides are present in the final product. A good catalyst should, in fact, not contain more than 5-8% Fe based on the total iron present. The value of "total reduced iron" ("Reduktionswert") was used to control the reduction. It should not exceed 65-75%. This value is determined by using 2% acetic acid. The catalyst is cooked 1½ hours in an excess of this acid. Fe and FeO dissolve, the remainder represents the unreduced iron oxide.

In starting a new batch, the catalyst is operated using watergas at minimum pressure at 130° C for ½ to 1 day. Following the "forming" the temperature and pressure are raised to operating level. The CO_2 usually added before shipment must be added very carefully to avoid overheating, since the heat of adsorption is very high.

The wax yield over this cycle depends largely on the proper KOH content (3.0%) of the fresh formed catalyst. The operating conditions for wax production are identical to those given under Lurgi Kreislauf operation and may be noted there.

(6) Brabag.

The entire research and commercial installations of this company connected with FT work are located at Ruhland-Schwarzheide and were not available to the members of this investigating team. No first-hand information regarding their development was obtained.

It is however known that Brabag had developed Fe catalysts. The catalysts are of the precipitated carrier type. Watergas was used and consumed in the ideal ratio. With this gas a three month catalyst life was obtained. The catalyst had to undergo "forming" which required 3-4 days with a space velocity of 10 V/H/V.

I.G. FARBENINDUSTRIE A.G.

I.G. had done considerable work on Fe catalyst prior to 1938 and a good part of this work was made available during the USAC meeting in 1938.

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I.G. Farbenindustrie A.G. (Cont'd.)

The work was carried out separately in Leuna and Ludwigshafen. The Leuna group, headed by Dr. Herold, deviated from the Fischer-Tropsch Synthesis and developed the Synol process for the direct production of alcohols. In Ludwigshafen, Dr. Michael (under Dr. Pier) continued work on gas recirculation and liquid phase operation while Dr. Duftschmid (under Dr. Mueller-Conradi) also developed a liquid phase process. Dr. Scheuermann worked on precipitated Fe catalysts.

I.G. had also worked on cobalt catalyst prior to 1939 but apparently only to substantiate Ruhrchemie's claims. Even at the present time, the I.G. Oxo-synthesis was based on the standard cobalt catalyst of RCH.

In the iron field, however, I.G.'s work was original, particularly their work on fused and sintered catalyst of the ammonia type, with which I.G. had some 25 years of practical experience. It has been claimed that such catalysts cannot possibly be as active as the precipitated type and thus had to operate at higher temperatures. Nevertheless I.G. was able to use their "MK 17", a sintered catalyst in the synol process, which operates at very low temperatures.

I.G. has done much work to develop methods for carrying out the synthesis in systems other than the plate or tube type reactors. None of these processes had reached commercialization. This may be due to the war and to the fact that I.G. with their high pressure hydrogenation had found better means to produce high quality motor and aircraft fuels and thus had only limited interest in the process.

The Synol unit, however, had been developed to a point where construction of a large plant had actually been decided upon. This is described in Section II, of this report.

(7) I.G. Farben Leuna.

Contrary to I.G.'s work on cobalt catalysts there were not many detailed catalyst studies made on iron catalysts. The effect of variations in operating conditions as studied on a number of Fe catalysts particularly the regular ammonia catalyst used in this plant. The influence of the temperature of reduction was studied on a fused iron ammonia type catalyst. The operating conditions in each case were identical, using watergas as feed.

(7) I.G. Farben Leuna (Cont'd.)

Reductions carried out with hydrogen at 1 atm. and 100 V/H/V.

Temperature of Reduction	Length of Reduction	Yield
850° C	16 hours	63 g/m^3 ideal gas
500° C	10 days	79 "
450° C	11 days	102 "
420° C	4 days	105 "
400° C	10 days	105 "

At lower reduction temperatures the activity rises, with a special sharp increase near 500° C. The extent of reduction (calculated from the water formation) is apparently only a secondary influence. If the H_2 is carried out at elevated pressure, the reduction can be completed even at low temperatures (200 atm. H_2, 300° C, 40-60 hours)

In accordance with all other observers, it was found that increased space velocity and higher temperatures in the synthesis increased the yield of lower boiling products. The reduction temperature, however, influenced the spectrum of the product differently, i.e., low reduction temperature gave low boiling products (all other conditions being equal). It appears that the reduction at lower temperature increases the hydrogenation capacity of the catalyst, which in turn increases the production of low boiling products.

The effect of space velocity was studied using a 15 mm. diameter tubular reactor. Space velocities (VHV) from 100 to 600 were used with 400 V/H/V determined as the practical limit. At higher velocities the catalyst had tendencies to coke up (by CO decomposition) due to local overheating. By taking good care, 500-600 V/H/V were reached for limited intervals. The actual overheating of the catalyst due to the high load is considered the cause of the increase in light products. With higher temperature and higher space velocity, somewhat more branched hydrocarbons were produced but the effect was not very pronounced.

The kinetics of the FT synthesis were formulated by I.G. chemists as follows:

(a) $CO + 2H_2 \longrightarrow CH_2 + H_2O$ Formation of methylene
By way of carbide formation and hydrogenation of the carbide.
(b) (1) $n\,CH_2 \longrightarrow (CH_{2\,n})$ polymerization of methylene
(2) $CH_2 + H_2 \longrightarrow CH_4$ Hydrogenation of methylene

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(7) I.G. Farben Leuna (Cont'd.)

(c) (1) $(CH_2)_n + H_2 \longrightarrow C_n H_{(2n+2)}$ Ending of polymerization due to hydrogenation of olefine.

(2) $CH_3(CH_2)_{n-3}CH{=}CH_2 \longrightarrow CH_3)CH_2)_{(\frac{n}{2}-2)} CH{=}CH(CH_2)_{(\frac{n}{2}-2)} - CH_3$

Ending of Polymerization due to shifting of double bond to middle of molecule.

It is obvious that the composition of the final product depends on the relative velocities of these reactions and thus on the relative rates of change of these velocities with change in temperature. It should also be noted that iron catalysts have apparently a good activity corresponding to reaction (C)(2).

Another reaction, not shown here but of interest would be the isomerization to branched chain hydrocarbons. The ability to catalyze this reaction is unfortunately not too good.

It was found that structurally there is little difference between gasoline synthesized over iron and over cobalt. The first gave much more olefines, but upon hydrogenation both gasolines showed the same octane number.

It is still possible to find two "Fe gasolines" with the same olefine content which differ in octane rating due to shifting of the double bond. It may be possible to develop a better control of these different reactions and thus produce a product of substantially only one type of hydrocarbon. Lastly there is still another reaction which is apparently the basis for the Synol process, i.e., the saturation of the terminal double bond with H_2O to form an alcohol. The process is described in Section II.

Carbon deposit is a well known occurence over Fe catalyst. It is due to the fact that Fe catalyzes the reactions.

(a) $2\,CO \longrightarrow CO_2 + C$

(b) $4\,CO + 3\,Fe \longrightarrow Fe_3O_4 + 4\,C$

I.G. checked this by determining the ratio Fe/Fe_3O_4 in a new and coked Fe catalyst. The ratio had shifted toward an increase in Fe_3O_4. In X-ray photographs the carbon did not appear indicating amorphous carbon. The newly formed Fe_3O_4 is very finely divided compared with the large crystals of Fe_3O_4 in the fresh catalyst.

RESTRICTED

(8) I.G. Farben-Ludwigshafen.

Waelsgas Process. (See reference I(b)/8, I(b)/9 and I(b)/10 at end of this section).

The gas circulating process (Dr. Michael) was well known before 1938 and had been discussed with U.S. representatives at the time. Dr. Michael used his sintered catalyst prepared by treating pelleted Fe powder (from carbonyl) with K_2CO_3 solution and sintering in H_2 atmosphere at 800-850° C for 4 hrs. The catalyst was actually iron carbide. But no exact work on the different carbides appears to have been carried on. The catalyst was not active requiring a temperature of 325° C for a 75% conversion.

When it became apparent that the process could not compete with high pressure hydrogenation in the production of high octane gasoline, it was decided to develop a process for the production of chemicals particularly olefines. The sintered catalyst was abandoned and replaced with a precipitated Fe catalyst. This catalyst did not have the mechanical strength required in the "Waelzgasprocess" and the process was abandoned. All further work carried out by Dr. Michael centered around operation in liquid phase and is described in that section.

For ready reference a set of operating data is listed below:

Reactor:	4 m^3 sintered Fe catalyst
Temperature	325° C
Pressure	20 atm.
V/H/V	250
Feedgas	CO: H_2 = 4:5 (17% inert)
Catalyst yield	0.7 Kg/liter catalyst/day

Product Distribution:

C_2H_4	8%
C_3H_6	9%
C_3H_8	3%
C_4H_8	8%
C_4H_{10}	2%
Gasoline 200° C	48%
Diesel oil 200-350° C	14%
Wax	1%
Alcohols	7%
TOTAL	100%

22 pts. of methane-ethane are also formed for 100 pts. of the listed products.

(8) I.G. Farben-Ludwigshafen (Cont'd.)

The gasoline must be refined (dehydration of alcohol) to remove oxygen. This causes about 6% loss. The treatment is carried out at 380° C over alumina. The treated gasoline has a Res. O.N. of 84. The diesel oil is ready for use, cetane number 50-55.

A horizontal reactor has been proposed to carry out the synthesis containing 20 m^3 of catalyst arranged in 4 separate horizontal layers of 250 mm. thick. Two reactors of this type would yield 10,000 ton/year of FT product. Note that this daily production per unit catalyst volume is about three times that reported in commercial FT operation. This is due to the higher space velocity, but the data should be used with caution.

A fairly detailed cost estimate for a 100,000 ton/year plant had also been worked out. The detailed figures may be taken from the attached report by Dr. Michael. The cost figures given are very nearly the same as these listed by Lurgi for a conventional FT plant using Fe catalyst and gas "Kreislauf".

Basis: RM/1 yearly ton total product	Synthesis & recovery	Total Plant
I.G. (Waelzgas unit)	243.-	865.-
Lurgi (Kreislauf)	290.-	590.-

(9) Comparative Tests with Fe Catalysts.

In the above sections, development work on Fe catalysts by different companies has been described. The reader may find it difficult to compare the results of this work, since each investigator is inclined to report in a different manner and also because the main objective of research may have been varied.

Apparently the German government felt the same way. Furthermore, it believed a decision regarding the use of Fe catalyst, at least in the three MP synthesis plants had to be made. To settle the argument, a set of tests in which each participant furnished his catalyst and operating personnel and using the same pressure and temperature was conducted by the government. The tests were carried out in the winter of 1943/1944 at the Brabag plant in Ruhland. (See reference I(b)/26 to I(b)/33 at end of this section.)

The participants were:

Ruhrchemie	I.G. Farben
Lurgi	Rheinpreussen
Brabag	Kaiser Wilhelm Institut

(9) Comparative Tests with Fe Catalysts (Cont'd.)

Appended to this report is a set of charts giving the operating data of each tests and the comparative yields. In addition, there is a copy of the report of each participant, after completing the test and comparing his own results with that of the others. Little work was carried out after completion of these tests and the results therefore represent the present state of German development of iron catalyst.

Note however that the range of operating conditions were not too wide and better results undoubtedly could have been obtained, if no limitations had been imposed. The arrangements for the tests were as follows:

Each reactor consisted of one double tube containing 4.8 liters of catalyst (O.D. 44 mm. I.D., 24 mm. height 4½ m).

The fresh feedgas (identical for all units) had a $CO:H_2$ ratio 1:1.25 (watergas) and 12% inert. S content under 0.1 gm/100 m^3.

The product recovery was conventional. The analytical methods are described in the attached report. The catalysts used by the participants are listed below. It was of importance to the Germans that the catalyst would be produced in one of the existing plants and did contain a minimum of critical materials, such as copper ("Sparmetalle").

COMPOSITION OF Fe-CATALYSTS FOR "R.A. VERSUCHE"
(All quantities based on 10 m^3 Cat. volume)

Catalyst	Fe Ton	Cu Kg	Alkali %	Carrier	"Forming" (Reduction)
K.W.I.	6	60	1% K_2CO_3 Basis Fe	None	Watergas
LURGI	3.9	390	30% K_4SiO_4 9% K_2O Basis Fe	SiO_2 (Waterglass)	Hydrogen 30% reduced
BRABAG	6.9	690	0.5% K_2CO_3 Basis Fe	None	Watergas 245° C H_2 or Sygas: 225°
I.G.	18.0 (fused iron)		1% K_2CO_3 Basis cat.	Al_2O_3CaO 2% max.	Hydrogen at 500°C
RUHRCHEMIE	2.5	125	0.5-2% K_2CO_3 Basis Fe	Kieselguhr	Hydrogen
RHEIN-PREUSSEN	2.7	135	0.5-1% K_2CO_3 Basis Fe	Ground Dolomite	Hydrogen 3-400° C Watergas 245° C

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(9) Comparative Tests with Fe Catalysts (Cont'd.)

It may be seen that the composition does not vary greatly. Lurgi used a somewhat higher alkali content. At the same time the yield of oxygenated compounds was highest over this catalyst. The catalysts vary however in regard to their apparent density as shown below:

I.G.	2.27	("Schuttgewicht" Kg/lit.cat.vol.)
Brabag	1.37	" "
K.W.I.	1.02	" "
Rheinpreussen	0.68	" "
Lurgi	0.79	" "
Ruhrchemie	0.44	" "

I.G.'s catalyst is fuzed, hence the high density. Brabag and K.W.I. use no carrier, while the three others use different type of carriers. Assuming that Fe is the only really active ingredient, it is of interest to note that the great variance in iron content had but little effect on the space velocity and specific output of the catalyst.

From the attached data sheet it can be seen, that based on 10 m^3 catalyst volume (standard FT reactor), a daily yield of 2.55 tons to 1.93 tons of C_3+ products was obtained by the six participants. This figure compares favorably with LP cobalt operation. The yield based on feed (88% $CO+H_2$) Watergas was from 99.5 to 87.4 g/m^3.

Oxygenated compounds are excluded in these yields. The operating pressure was identical (10 at) in all cases. The temperature and V/H/V were up to the individual operator. At the end of two weeks all units had reached around 220° C. The space velocities varied between 105 to 110 on the average. A summary of the results is listed below:

	KWI	LURGI	BRABAG	I.G.	RCH	Rh. Pr.
GAS (C_1+C_2)	16.6	10.8	8.4	16.8	13.6	17.1
GASOL (C_3+C_4)	19.9	12.3	9.8	18.1	14.3	21.5
GASOLINE (C_5-C_{10})	25.1	19.5	17.9	25.7	22.3	29.8
DIESEL OIL ($C_{11}-C_{18}$	14.0	13.1	16.4	11.5	12.7	13.7
GATSCH (320-450°C)	7.9	8.2	12.6	6.1	7.1	6.3
HARD WAX (450°C)	10.3	27.0	30.8	14.8	18.7	6.3
LOW BOILING ALCOHOL	6.11	9.2	4.1	7.0	11.3	5.3

(Cont'd)

(9) Comparative Tests with Fe Catalysts (Cont'd.)

	KWI	LURGI	BRABAG	I.G.	RCH	Rh. Pr.
TOTAL ALCOHOL	7.0	14.4	9.5	10.7	15.8	7.5
TOTAL ESTER	1.1	8.0	2.7	1.7	2.6	0.3
TOTAL OLEFINE	25.9	30.4	34.2	39.1	26.1	29.7
Tons/day TOTAL	3.26	3.19	2.88	3.2	2.47	2.6
g/m^3 Sy. gas TOTAL	125.2	124.2	108.3	117.1	103.1	104.0
g/m^3 max. Value	147.3	142	141	144	147	168
$CO:H_2$ Consumed Ratio	0.80	0.66	0.69	0.74	0.72	1.07 ($CO:H_2$ feed 1:1.25)
CO Conversion	85.0	88	77	81	70	57

The products vary within a reasonable range: Lurgi + Brabag gave the most hard wax, one of the objects of this race. Rheinpreussen produced a very light product, which might be considered a failure. I.G. and KWI apparently produced the most olefines. The gasolines varied only little among themselves and also if compared with an LP cobalt gasoline. (See report of Analysis by KWI). The waxes were tested for their use as feed to oxidation plants. No definite conclusions were reached on the subject, but it was feared that the wax paraffins might be too highly branched.

Only three of the six catalysts operated 90 days with the first batch catalyst. The others ran into coke trouble and had to renew the charges repeatedly (4 times in the case of Rheinpreussen), before the required 90 days run could be completed. This was a serious drawback. If the catalyst could not be prepared with sufficient assurance that coke deposit would not occur, it could not be considered ready for commercial application. (Coking of an FT oven is a serious problem requiring a shutdown of several weeks for cleanout).

The important fact about these tests is apparently that all participants obtained reasonably good results, under conditions similar to those used in MP cobalt operation with a set of greatly different Fe catalysts (great difference in Fe content). Another fact is the general use of copper and alkali to promote the catalyst.

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(9) Comparative Tests with Fe Catalysts (Cont'd.)

Liquid Phase Operation

The idea of conducting the FT synthesis in liquid phase is not new as it had been attempted a long time ago by Fischer. Today, it is considered as promising and research on the subject was carried out notably by I.G. Farben, Ruhrchemie, and Rheinpreussen. The easier control of the reaction temperature is the main incentive for the use of such a system. The main drawback, if any, is the probably loss in catalyst efficienty, a point which is not yet clear. Three types of operations were tried:

(a) "Oel Kreislauf": The use of a solid catalyst bed with the oil being circulated over the catalyst concurrently with the gas.

(b) "Schaumfahrweise" Suspension of the catalyst in the oil phase and dispersion of the catalyst by the gas using a ceramic disc or mechanical stirrer. The heat of reaction is removed by circulating the slurry through an external cooler.

(c) Static liquid phase: Similar to (b), but the heat of the reaction is removed by a set of cooling tubes which are inserted in the liquid.

Systems (a) and (b) were used by I.G. Farben and system (c) by Rheinpreussen.

(10) "Oilkreislauf" Process - I.G. Farben.

(See reference I(b)/11, I(b)/12 and I(b)/13 at end of this section)
The catalyst used was of the fused iron type (ammonia catalyst). It was obtained by melting pure iron powder (from carbonyl) with O_2 and adding certain promoters. The melt was then broken into particles from 8-15 mm. size and arranged in a reactor as a solid bed. A 500 mm.chamber, 6 m. high was used in the tests.

The oil used for circulation is the product of the synthesis itself, sp. gr. 0.8 - 0.81, conditioned by distillation to keep it within any specified boiling range. The use of the oil prohibits the development of any local hot-spots and thus lowers the yield of gaseous products.

The operating results were as follows:

Pressure	25 atm.
Temperature	300° C (approximately)

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(10) "Oilkreislauf" Process - I.G. Farben. (Cont'd.)

Space velocity	200 V/H/V (apparent catalyst density 2.5)
Yield	150 g/m^3 total product/basis ideal gas
Conversion	87%
Output	7.2 ton/10 m^3 catalyst volume.

Product Distribution.

Gasoline	40% (50% olefine, 2% oxygen, ON65)
Gas Oil	20% (40% olefine, 0.6 - 1% oxygen)
Hard Wax	20 (95° C melting point)
$C_3 + C_4$	15 (75% olefine)
Alcohol	5% (mostly ethylalcohol)

Olefines boiling above 100° C consisted of 50% normal and 50% iso-olefine (no data were given for the paraffins).

The most important fact is the high space velocity and resulting high production from a given catalyst volume. It is furthermore a considerably simpler and thus cheaper method, than the customary synthesis.

The cost for a 100,000 ton/year plant was given as RM 5,720,000 (RM 57.2/yearly ton) as compared to RM. 243/yearly ton for the gas circulation process (I.G.) or RM 290/yearly ton for a regular FT plant (Lurgi) with Fe catalyst and "Kreislauf". This figure appears quite out of line. The difference may be due to the exclusion of certain auxiliary equipment.

The use of the "Oilkreislauf" was later considered for the production of alcohols. In particular alcohols in the $C_9 - C_{12}$ range were desired for detergents and chemicals. To this end tests were run with the system at elevated pressures (100 and 180 atm.) but the results were negative since the product was quite low boiling.

(11) "Schaumfahrweise" Process - I.G. Farben.

(See reference I(b)/18 to I(b)/22 at end of this section).
This process was developed by Dr. Michael after abandoning the gas-recycle principle.

It is quite similar to the "Oelkreislauf" process except for the handling of the catalyst. The latter is here held in suspension in the liquid by the gas bubbling up through the reactor. It was desired to operate in a system where the catalyst was dispersed widely and in direct

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contact with the gas if possible. An attempt to obtain this result by dispersing the gas to give a regular froth was made using the product of the synthesis as liquid phase and forcing the gas through a ceramic disc or nozzles with very fine pores to give the necessary dispersion.

The heat of reaction is removed by circulating the slurry through an outside cooler. For this purpose the reactor is allowed to overflow into the settling vessel where the unreacted gas carrying the light product, vapor is released and withdrawn. The slurry is then passed through the cooler and then picked up by the circulating pump. The net excess product boiling within the range of the circulating oil is withdrawn.

Preliminary tests were carried out in a reactor 500 mm. diameter x 8.0 m. high (1.5 m^3 reactor volume). Some initial difficulties, such as wear in the slurry pump, could be overcome by use of flushing oil in the stuffing box. The oil velocity required for good operation was such as to give 20 changes of oil per hour in the reactor.

Some difficulty was also encountered with the dispersion plate. The feed gas had to be heated to prevent thermal stress and rupture of the disc. A chamotte plate showed good stability. A disc with 0.1 mm. pore size gave good reactor output but resulted in 5 atm. pressure drop. A 0.2 mm. pore size was substituted resulting in a pressure drop of 1 atm. but causing at the same time a drop in output of 25%. Apparently the dispersion depends greatly on the pore size.

No emulsifiers were used in the system but certain of the liquid oxygenated compounds gave such an effect.

In one test the catalyst, after 8 weeks, began to produce increased amounts of low boiling products and less wax. This could have been caused by sulphur, but it could have been due to the extraction of the alkali in the catalyst by the fatty acid formed in the synthesis.

Upon continued operation (3 months) increased losses of catalyst were noted, which could not be explained by the mechanical losses such as pump leaks or entrainment. Upon inspection it was found that the catalyst had formed a solid cake around the wall of the oven (4 cm. thick) particularly in the upper section of the vessel. The catalyst had also settled out in the gas separator. The deposit was thoroughly analyzed and was found to have the following composition: (next page)

(11) "Schaumfahrweise" Process - I.G. Farben (Cont'd.)

$FeCO_3$	48.20% wt.
FeO	13.40 "
Fe_2O_3	0.25 "
Fe_2C	8.50 "
Fe metal	20.30 "
Free carbon	5.10 "
S (Sulfide)	0.03 "
Other	8.81 "
TOTAL	100.00% wt.

The high Fe CO_3 content is due to the high CO_2 content of the exit gas (partial pressure $P_{CO_2} = 6-8$ atm) reacting with FeO. It was further concluded, that some gum-forming substance had served as a glue to hold the catalyst on the wall. Studies to analyze this material were under way.

(a) Catalyst.

The catalyst was prepared by decomposing iron carbonyl, 1% alkali was added. After reduction the catalyst was ground in oil to 1-5 m particle size. The concentration in the liquid was 300-400 Kg/m^3.

The catalyst operates at comparatively low temperatures and the amount of gas formed is small. At 70% conversion, the gas analyses are as follows:

	Feed gas	Tail gas
CO_2	0.8%	30.4%
C_mH_{2n}	-	3.0
H_2	42.5	31.1
CO	53.6	27.8
HC^s	1.0	3.7
N_2	2.1	4.0

It is therefore possible to remove the CO_2, and return the tailgas to the reactor without at the same time diluting the feedgas with inert components, thereby the ultimate conversion could be increased to 90%.

The capacity based on reactor volume varied with temperature. For operation at 20 atm. the following figures were given:

Temperature	Space Velocity
250°	80 m^3 gas/m^3 reactor
275°	125 " "

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(11) "Schaumfahrweise" Process - I.G. Farben (Cont'd.)

Note: That the space velocity is again in the same range as in ordinary FT operations. For 100,000 ton year primary product, 950 m^3 reactor volume are required according to Dr. Michael corresponding to 2.9 ton/day/10 m^3 catalyst.

PRODUCT DISTRIBUTION

Boiling Range	% Weight	% Paraffin	% Olefine	% Alcohol	% Acid & Ester
1 - 50° C	4	12	85	0	3
50-100°	20	7	83	5	5
100-150°	16	11	67	15	7
150-200°	10	20	62	12	6
200-250°	12	17	63	12	8
250-300°	10	25	54	10	11
300-350°	8	38	45	5	12
+350°	20	-	-	-	-

Note the high content of olefines and oxygenated compounds.

For commercial practice a 12-15 m^3 oven was considered practical. No plant costs had been calculated for this type of unit but for a 100,000 T/year plant the following utilities were required. (This includes complete plant and product recovery).

Steam	12.5 ton/hr.
Water	3500 m^3/hr.
Power	3120 KW
Fuel	2 x 10^6 K cal/hr.
Labor	71 men/shift.

(b) Products.

The high olefine content makes the product suitable for chemical synthesis. The $C_3 - C_4$ fraction may be polymerized.

The gasoline can be refined for removal of oxygenated products in the conventional manner of bauxite.

Octane rating of treated gasoline:	70 (Research) for 250° temperature. 75 (Research) for 275° Synthesis.

(11) "Schaumfahrweise" Process - I.G. Farben (Cont'd.)

The removal of oxygenated compounds is an important step if the fractions are to be used for polymerisation (with $AlCl_3$) or for the Oxo process.

The middle oil has a cetane number of 70 and may be used directly, but it is of course the preferred feed for lube oil synthesis and the Oxo reaction.

The wax may be cracked to give a 70% yield of olefinic middle oil. Before it can be used for oxidation it is necessary to hydrogenate the olefines and at the same time remove the higher alcohols and esters.

About 70% of the total wax is hard wax with a melting point over 80-90° C.

(12) "Static Liquid Phase" Rheinpreussen.

Aside from I.G. Farben the attempt to operate in liquid phase was also made by Rheinpreussen. Their work on liquid phase operation did not leave the laboratory stage. The reaction was studied on a small scale and appeared quite successful. A pilot plant was designed employing a new type of reactor and the unit had been assembled for the most part when the progress of the war stopped further work.

The system employs a slurry of catalyst in the reaction products, the catalyst being held in suspension by the rising bubbles of the feedgas. Contrary to the Michael process the slurry is here not circulated through a cooler but forms a static layer. The heat of reaction is removed by a cooler consisting of a multitude of tubes hung vertically in the reactor. The details are described in the following section of new reactor design.

The net product of the synthesis boiling within the range of the slurry oil would have to be withdrawn from the reactor and filtered to remove the catalyst. This filtration problem has been the subject of a special study carried out by Rheinpreussen.

The catalyst in these studies was prepared from Luxmasse (the same material as is used for the "Grobreiningung". The raw mass is thoroughly washed with water and then alkalized with K_2CO_3. Finally the catalyst is ground in Kogasin to give a fine suspension. The density was around 7 g Fe in 12 liter suspension (3.5% slurry). Here too it was found that the K_2O content of the catalyst apparently dropped during operation. It was attempted to correct this by adding K_2CO_3 in powder form to the slurry, but without success.

(12)"Static Liquid Phase" Rheinpreussen (Cont'd.)

After a certain time the catalyst slurry was withdrawn, filtered, and the wax extracted, but this treatment also seemed to have little effect.

Other catalysts, with and without carrier were studied in this system. Carriers appeared to give a lower boiling product, no wax. In one case no liquid buildup was noticed for a period of 670 hours.

Before putting such a unit on stream one of the main problems is the necessity to keep the slurry from settling. It may be necessary to use N_2 or CH_4 to do so before the synthesis gas is admitted.

The following results were given for operation with slurry catalyst in the laboratory.

Feedgas	$CO = 40\%$; $H_2 = 44\%$
Forming of catalyst	(a) Heating slurry (with N_2 flowing) to 278° (b) Form with CO containing gas at 250° for 10 hrs. (c) Put on stream: rate 6 lit/hr feed/10 g Fe.
Conversion	94% CO
Absorber 60° C	12 gm/m³ $CO+H_2$
Light oil 60-280°C	38 "
Heavy oil 280° C	65 "
C_3+C_4	9 "
CH_4	2 "
	126 gm/m³ $CO+H_2$

This operation appears of great interest and it was regarded as highly promising by the Rheinpreussen engineers.

(a) Ruhrchemie.

Ruhrchemie had done some work on liquid phase operation early in the war. The work apparently had not reached the stage of large scale pilot plant operation. A patent had been applied for operation in liquid phase on 10 March 1941.

According to this claim the operation was to be carried out by passing the feed gas through a catalyst slurry. RCH considered it essential to operate at high space velocity, about 200-700 V/H/V. Under these conditions the conversion was around 50%. This led to the use of a multistage process. The conversion was in fact governed by the amount of CH_4 formed in the synthesis. A maximum of 1% CH_4 formation was to be allowed in each stage.

(12) "Static Liquid Phase" Rheinpreussen (Cont'd.)

The underlying thought is the assumption that in all liquid phase operations the higher boiling products are in danger of being cracked due to the much longer contact with the catalyst. Not enough practical experience on liquid phase operation is available as yet to study this effect.

Another RCH patent application dated 7 July 1941, was supposed to cover operations with liquid injections as means to remove the heat of reaction. This operation also is not new, but was not carried out in any large scale apparatus. The injected liquid is evaporated and the quantity used in such that the heat of reaction balances the latent heat of the injected liquid. It appears that the quantity of liquid required might be quite substantial and RCH visualized a stepwise operation with condensation between each stage.

No operating data on RCH liquid operation were obtained.

(13) New Reactor Design - General.

There has been practically no new development in this direction that has reached commercial application with the exception of the "Taschenrohr" oven at Krupp's plant in Wanne-Eickel.

All existing LP plants use the standard plate-oven. The MP plants employ the double tube reactor which has been described in detail in the literature, and at Schaffgotsch some single tube reactors were used. However, parallel with the development of the Fe catalyst, there were attempts to improve the reactor.

The following improvements are noted:

(a) Krupp Taschenrohrofen.
(b) Lurgi MP reactor.
(c) I.G. MP reactor (for Synol plant).
(d) Rheinpreussen liquid phase reactor.

Empty vessels as are required in the I.G. "Waelz" or "Oelkreis" process are not considered here.

(a) "Taschenrohrofen". (See reference I(b)/39 at end of this section).

This oven is a regular MP Fischer oven. Instead of using the conventional double tubes, the tubes are large and contain a number of internal

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tube fins, which intersect the tube in such a manner that no catalyst particle is more than 5 mm. from the nearest fin or tubewall. 16 ovens of this type were installed in the 2nd stage of the Krupp plant at Wanne-Eickel. (There were also 8 regular double tube ovens in the plant).

A detailed drawing of the oven is attached. Each tube 75 mm. diameter and 3750 mm. long, contained 0.01275 m^3 of catalyst, the entire oven contained the conventional 10 m^3. The watercooled surface is 0.85 m^2/tube (670 m^2/oven). The finned surface is 2.13 m^2/tube (1670 m^2/oven.)

It was stated that the catalyst was not easily removed from these tubes. The capacity of the oven as a unit was comparable to the double tube oven.

(b) Lurgi M.P. Oven. (See reference I(b)/42 at end of this section).

The use of Fe catalysts required the construction of ovens which could stand the 20-30 atm. pressure on the catalyst side and at the same time the somewhat higher pressure on the steam side (up to 60 atm). The arrangement proposed by Lurgi consisted simply of the conventional LP plate oven installed on a horizontal HP drum. One head of the drum is flanged and the cooling coil is connected to that head. For filling and removal of the catalyst, the flange is opened and the head with the entire catalyst and cooling system is drawn out of the pressure drum.

The plate bundle itself is enclosed in a thin sheet jacket to prevent flashing of the pyrophoric catalyst, when the bundle is drawn. The same difficulties in filling and removing of catalyst usually experienced in the LP oven will have to be met in this design.

A pilot unit of this type, containing 7 m^3 catalyst and operating at 20 atm. was installed at the gasworks near Boehlen-Rotha. The unit was to be studied for possible use in detoxification of city gas (and of course, FT). Only one run had been made at the unit and the oven apparently performed well. No detailed operating data were available, but the pilot unit had been designed to operate at space velocities up to 400 V/H/V (including recycle gas). The gas enters the top of the basket containing the catalyst and passes down through the bed. The bottom of the basket is connected to the exit nozzle of the pressure vessel by means of a special expansion joint.

(13) New Reactor Design - General (Cont'd.)

(c) I.G. Farben Synol Reactor. (See reference I(b)/41 at end of this Section).

This oven was developed to carry out FT reactions and related synthesis. Considerable work was done by I.G. engineers to arrive at a theoretical basis before selecting a reactor for these exothermic reactions. Three possible arrangements were considered. (See report by Dr. E. Wirth of April 1942, Leuna., Reference I(b)/34 to I(b)/37 at end of this section).

(1) Catalyst inside the tubes.
(2) Catalyst between plates.
(3) Catalyst outside the tubes.

The following general conclusions were drawn:

(a) The catalyst in tube arrangement required the largest cooling surface and, based on total reactor-volume, contains the least amount of catalyst. But it may be arranged to give tall catalyst layers should that be required.

(b) The catalyst outside the tubes is superior to the reverse arrangement and the improvement becomes greater as the diameter of the cooling tubes decreases. Structural difficulties apparently are the main drawback

(c) The plate reactor is also superior to the catalyst tube reactor. But for increased heats of reaction (or better for increased heat release per m^3 of reactor), less control is afforded by the plate oven, as a substantial temperature gradient develops across the plate.

These conclusions may be only of theoretical interest and are of course based on arbitrary assumptions. Particularly, on the assumption that the heat transfer coefficient between surface and catalyst is the same. This is hardly the case as this coefficient varies with the direction of flow, which may be at a right angle to the tubes in the case where the catalyst is arranged outside the tube.

It was found that the plate-oven required 71%, the catalyst outside-tube oven only 60% of the surface necessary in the catalyst in tube type for the same temperature difference (ΔT) throughout the catalyst. For varying ΔT, it appears that the specific cooling surface of the catalyst outside-tube oven depends largely on the tube diameter used in the design and the larger the ΔT, the more apparent is this advantage over the catalyst in tube type.

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(13) New Reactor Design - General (c)(Cont'd.)

An example may illustrate this:

An oven containing the catalyst in 20 mm. tubes is operated to give a certain Δ T max. through the catalyst. The surface required is to be 100%. A plate oven, in order to give the same ΔT would require 71% of the cooling surface (actually 77%, since the surface of the tubes traversing the plates must also be counted). An equivalent "catalyst-outside-tube-oven" using 50 mm. tubes would require 75% of the surface but if 20 mm. tubes are used only 63% of the surface is required. If however the "basic" catalyst in tube oven were using 50 mm. tubes (indicating a higher Δ T is permissible), then the surface for a plate oven would still be 77%, but the catalyst outside tube oven employing 50 mm. tubes would need only 65%, and if 20 mm. tubes were used only 52%. Thus the advantage becomes more apparent as the heatload decreases.

The design of the furnace, finally proposed for the plant, may be seen from the attached drawing M 4949-1 (Ammoniakwerk Merseburg) and a patent application. The tube bundle consists of a multitude of bayonet type tubes closed on one end. The circulation could be forced, but it was considered preferable to install the oven at a slight incline (6°) to induce natural circulation. In order to find the minimum angle required for adequate circulation, tests were carried out to establish the velocities of air bubbles in water ascending in an inclined tube as function of the angle. This report is attached. It was determined that a 6° angle gave sufficient flow. The oven otherwise resembles closely the Lurgi reactor, in regards to catalyst arrangement, pressure and general layout. The catalyst is again enclosed in a sheet iron box.

One of the major advantages in the design of this furnace is the simple filling and removal of the catalyst since no plates are used. The commercial oven was to contain 6.8 m^3 of catalyst. The 18 mm. O.D. tubes were arranged in 28 mm. triangular spacing giving a total of 800 m^2 cooling surface per oven. Results obtained on this type reactor are described in the section of "Synol".

(d) Rheinpreussen Liquid Phase Reactor. (See reference I(b)/40 at end of this section).

(1) This oven has been mentioned above in connection with Rheinpreussen liquid phase development. See also the attached Rheinpreussen drwg. 45099.

(2) The reaction is carried out in liquid phase. The slurry is contained in a vertical pressure vessel 1500 mm. diameter and 9560 mm.

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(13) New Reactor Design - General (d) (Cont'd.)

high, (when filled with 10 m^3 of catalyst slurry, the height of the liquid is 8060 mm.) Gas is introduced through the bottom by way of a multitude of ceramic discs, thimbles, or similar means. The heat of reaction is removed by a tube bundle consisting of a multitude of vertical bayonet tubes. The top head of the vessel can be removed to draw the bundle. The bundle has a total surface of only 350 m^2, which is considerably less than the required in gasphase operations.

(3) Horizontal oven. Another pilot plant reactor had been installed by Rheinpreussen but never put into operation. The furnace is similar to the one used by Lurgi consisting of a plate-tube bundle in a horizontal pressure vessel.

(14) List of References.

The German documents listed below are available in the library of the Bureau of Ships in Washington, D.C.

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2. Die Thermodynamik d.F.T. Synthese - by P. Dolch 2/19/44.
3. Die Berechnung von Gasverarbeitung bei der CO-Hydrierung - Dr. Roelen July 1944.
4. Ueber die Berechnung der Ausbeute bei der Synthese - by Dr. Roelen, August 1944.
5. Two drwg. Lurgi: DS am 103 and DS am 104, "Mitteldrucksynthese von Kohlenwasserstoffen".
6. Synthese hoeherer aliphatischer Kohlenwasserstoffe (patent application) KWI: 18 April 1941.
7. Aussprache: Vortrag ueber Fe-Katalysatoren bei der Mitteldrucksynthese KWI. 10 September 1940.
8. "Der derseitige Stand d. K.W. - Synthese aus CO-H_2" by Michael 6/27/41.
9. "Stand der Synthese nach dem Gasumwaelzverfahren" - by Michael 2/15/41.
10. "Verfahren Dr. Michael - Fahrweise auf Mitteloel" - 20 May 1940.
11. "CO+H_2 Synthese, Oelkreislaufverfahren" - By Duftschmid 25 July 1941.
12. "KW-Synthese aus CO+H_2 Oelkreislaufverfahren" - by Duftschmid 10/9/39.
13. Stand der Versuche zur Alkolsynthese nach dem Oelkreislaufverfahren - by Duftschmid 11 August 1941.

(14) List of References (Cont'd.)

14. "Zusammensetzung von 100,000 T Rohanfall bei I.G. Michaelverfahren" 3/12/40.
15. "Erfahrungen mit dem Syntheseofen, Kammer 506" - by Michael 28 June 1941.
16. "Synthese von Mitteloel und Paraffin mit Eisenkontakten" - by Michael 15 March 1941.
17. "Stand der Syntheseoelversuche" - by Michael 1 April 1942.
18. "KW Synthese aus CO + H_2 nach Schaumfahrweise" - by Michael 6/23/42
19. "Kohlenwasserstoffsynthese aus CO, H_2 Schaumfahrweise" - by Michael 25 June 1942.
20. KW Synthese Stand der Schaumfahrweise - by Michael 12 July 1942.
21. "Kontaktausscheidung an der Ofenwand" - by Michael 28 Nov. 1942.
22. "Besichtigung der Sumpfphase KW Synthese" - by Gemassmer 28 April 1943.
23. "Bericht ueber Arbeiten zur KW Synthese" - by Wintzer, March 1940.
24. "Sitzungsprotokoll" - 5 September 1944 (Reichamtsversuche)
25. "Normaldrucksynthese an Eisenkontakten" - by Koelbel 24 June 1944.
26. "Ergaenzungen zu den Bilanzblaettern" (RA-Versuche) - 5 June 1944.
27. A set balance sheets (Bilanzblaetter) Re: RA-Versuche) 9 schedules.
28. "Bericht ueber RA Versuche" - by Sauter-Brabag 21 August 1944.
29. "Auswertung der RA Versuche" - by Pichler. KWI 18 August 1944.
30. "Auswertung der RA Versuche" - by Herbert Lurgi, 5 August 1944.
31. "Stellungnahme der RCH zu RA Versuchen" - by Roelen, Ruhrchemie 8/26/44.
32. "RA Versuche an Fe Kontakter" - Wietzel I.G. Farben Lu. 25 August 1944.
33. "Bericht ueber Untersuchnung der Benzinfraktionen aus der RA Versuchen" - by Koch KWI, 1 May 1944.
34. "Verfahren zur Durchfuehrung exothermer Reaktionen" - patent application, I.G. Leuna 9 July 1942.
35. Durchfuehrung Chemischer Umsetzungen - patent application I.G. Leuna, 13 October 1942.
36. "Gestaltung des Kontaktraumes bei exothermen Reaktionen" - by Wirth April 1942.
37. "Berechnung von Oefen fuer katalytische exotherme Reaktionen in engen Temperaturgrenzen" - by Wirth 4 July 1942.
38. One drwg. Wintershall: 3326/A "Kontaktofen"
39. One drwg. Hoesch: 71-116 "Versuchskontaktofen".
40. One drwg. Mannesmann Werke/45099 "Probe Kontaktofen Rheinpreussen"
41. One drwg. "Ammoniawerk/M4949a-1 "Entwurf eines Synthese Kontaktofen"
42. One drwg. Mittel Stahl/5203-1 "Versuchsdruckofen System Lurgi"
43. One drwg. Lurgi OFT/145: "Schema der Versuchsanlage".

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SYNTHESIS OF HYDROCARBONS AND CHEMICALS CO_2 AND H_2

SECTION I (c)

1. General Introduction.

The attempts to convert CO_2 with H_2 is not at all new, but it is of interest to note that the Germans obtained fair results using the identical catalyst as in the FT synthesis.

The work was carried out at the "Kaiser-Wilhelm Institut" in Muelheim (KWI). The catalyst used was described in detail in Section 18. It had been carbided at 1/10 atm. with CO at 325° C. Alkalized and non-alkalized catalyst was used.

Since the temperature of the synthesis must be rather high, the product is usually methane and a few g/m^3 gasol. In fact the method was considered of interest mainly for the production of a standard city gas.

2. Operating Conditions.

Contraction data are given below based on feed gas: CO_2:H_2=1:3:V/H/V: 4 lit/hr/10 g Fe in catalyst.

	Non-Alkalized catalyst		1% K_2CO_3 in catalyst
Temperature	1 atm.	15 atm.	1 atm.
250° C	8	27	8
300° C	11	41	14
350° C	22	44	16
400° C	21	44	17
450° C	20	44	17

The influence of alkali is the same as in FT operation in that it raises the boiling range of the product. In this case alkali increases the liquid yield. Basis CO_2:H_2 = 1:3; 15 atm; 350° C, 2 lit/hr/10 g Fe.

% K_2CO_3	Contraction	g liquid/m^3	g gasol/m^3
0.0	30	3-5	1.5
1.0	40	16.0	11.0

2. Operating Conditions (Cont'd.)

Pressure increases the conversion. The following data show the contraction at different pressure:

Basis: Feed $CO_2 : H_2 = 1:3$; 350° C - 2 lit/hr/10 g Fe.

1% alkali in catalyst

Pressure	Contraction	g liquid/m^3	g gasol/m^3
15 atm.	40	16	11
30 atm.	47	24	15
60 atm.	58	39	23

Upon further increase in pressure the contraction began to decrease. Increased pressure also favors the synthesis of oxygenated compounds analogous to FT synthesis.

3. Reference.

The following German document is available in the library of the Bureau of Ships in Washington, D.C.

1. "Ueber die Umsetzung von CO_2 - H_2 Gemischen zu fluessigen und gasfoermigen Kohlenwasserstoffen" - by Dr. Pichler KWI.

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THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

SECTION II

THE SYNOL PROCESS

SUMMARY

The attached report covers the development of the Synol process by I.G. Leuna. The process involves the direct synthesis of higher alcohols from CO and H_2 over a specially reduced iron catalyst at medium pressure.

The products were considered of outstanding quality being almost exclusively straight chain terminal alcohols. They were considered for use in the manufacture of lubricating esters and detergents.

The development was carried through laboratory and pilot plant stage and construction of a 30,000 ton/year plant at Leuan was considered.

Contents:

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SECTION II

THE SYNOL PROCESS

1. General Introduction.

The synol process has been developed by I.G. Farben at Leuna under the direction of Dr. Herold. It is a new process for the production of oxygenated compounds, mainly alcohols. The hydrogenation of CO to form alcohols at high pressure is an established process (methanol synthesis and isobutanol synthesis). The synol process is one attempt to continue this series and produce higher boiling alcohols with the OH group in the terminal position, thereby differing from the α alkyl-alcohol of the oxo-synthesis and the branched chain alcohols of the isobutyl synthesis.

The overall equation of the Synthesis may be written as follows:

$$28 \ CO + 23 \ H_2 \longrightarrow CH3 \ (CH2)_8 - OH + C_8 \ H_{16} + 11 \ CO_2 + 5H_2 \ O$$

This result, the direction of the synthesis towards the production of alcohols, was obtained by operating at intermediate pressures over iron catalysts, and at the lowest possible temperatures, 180° - 200° C. This in turn is made possible by a special reduction of the catalyst.

The development of the process was carried out mostly during the war. A series of patents, covering the essential features, were applied for in Germany only. Towards the end of the war it was decided to build a 30,000 ton/year plant at Leuna, but the project was still in the paper stage when the war ended.

The basic patent (see reference II/2, II/3 and II/4 at end of this section) applied for in September 1942 makes the following claim:

A process for the production of alcohols from CO and H_2 over Fe catalyst at elevated pressure, characterized by the operation at temperatures substantially lower than those required for the production of hydrocarbons over the same catalyst.

The patent further discloses the use of excess hydrogen in the preparation of the catalyst and the importance of keeping any trace of oxygen from the catalyst during and after reduction.

In another patent application, dated March 1943, the use of gas recycle, with intermediate removal of the product, is disclosed as a means to increase the percentage of alcohols in the product to 70% and more. This is the same principle as the "Kreislauf" process for the increase of olefines.

2. Catalysts. (See also references II/26 to II/30 at end of this section).

(a) Preparation.

Fuzed as well as precipitated catalysts have been studied, but the ease in handling and reproduction and mechanical strength of the fuzed type led to the almost exclusive use of the latter. It is substantially identical with the Leuna ammonia catalyst. The catalyst may be prepared as follows:

Pure electrolytic iron or iron from carbonyl (99.9% minimum purity) was mixed with alumina to give a final mixture of 3.5% Al_2O_3 based on Fe, 0.15 to 0.5% K_2O are added and the iron is oxidized. If iron metal was the raw material, oxygen has to be used for the oxidation step. The exact final state of oxidation was not known, but the catalyst could be readily reproduced.

The melt is broken up into 1-2 mm. particles and reduced. The reduction requires hydrogen of high purity and a large excess of hydrogen is used. A temperature, however, of at least 420° had to be reached to obtain reduction.

Some X-ray studies had been made regarding the influence of the reduction temperature. It was found that at 400° C, Fe_3O_4 and Fe were present in the ratio of around 1:3. At 425° the ratio was nearer 1:4 while at 500° no more Fe_3O_4 could be found. By the same method it was further determined that the space velocity of the H_2 over the iron influenced the Fe_3O_4: Fe ratio. Thus: At 300 V/H/V, after 6 days, the ratio was still 0.75, but at 3000 V/H/V after 4 days it was 0.3

In a patent application, dated July 1941, the use of reduction with H_2 is disclosed, whereby the product of space velocity x time (days) must exceed 2000. This is apparently the lower limit.

(b) Reduction.

At the present time, the following conditions are used for the reduction:

2. Catalysts (Cont'd.)

Pure hydrogen (Sulphur - 0.10 gm/100 m^3) enters the system through a Pattenhausen grude tower to protect against break through of sulphur. The gas next passes a methanizer to remove traces of CO (the methanizer could however be omitted). The fresh H_2 is then added to the recycle, where it represents 3-5% of the total stream. The total hydrogen passes through silicagel drums, is dried and the dry hydrogen is blown through the preheater and the reduction vessel. The exit gas is cooled with water and NH_3 before being returned to the silicagel drier.

The reduction vessel (1400 mm. diameter) is filled with 500 liter fuzed Fe catalyst (0.5-1.0 mm.) The catalyst is retained on a bronze screen. Care is to be taken that no catalyst particles fall through the screen before reduction.

After thorough purging of the H2-circuit, the heater is fired and the temperature raised to 450° C within five hours. The dried H_2 is circulated at 2000 V/H/V.

The water content of this H_2 after drying is 0.5-2 gm/m^3. At the beginning of the reduction the H_2O content after the catalyst rises to a dew point of plus 4.0°C. Part of the water is condensed in the NH_3 cooler and the remainder is removed in the driers. A certain amount of NH_3 formed during the reduction is absorbed in the water.

The reduction is completed after 50 hours. The system is cooled and CO_2 admitted slowly to avoid overheating from the absorption of CO_2 on the catalyst. This CO_2 used for blanketing must be dried over silicagel and must be free of sulphur.

In handling, utmost care must be taken to prevent <u>all</u> oxygen from coming in contact with the catalyst. Even the slightest poisoning of the reduced iron with air or oxygen requires a higher initial synthesis temperature (less alcohols) and shortens the catalyst life. The apparent density of the finished catalyst varies from 1.8 to 2.2 according to particle size.

The life of the catalyst is around 9 months. For the design of a plant, which was to make catalyst for a 10,000 ton/year synolplant, an average life of only 4 months had been assumed. It is noteworthy that additions of several tenths of 1% of arsenic to the catalyst results in a substantial increase of esters (25% in the 200°-300° C fraction). In the synthesis the catalyst immediately forms Fe2 C of hexagonal crystal structure and above temperature of 290° C this carbide is converted to an inactive form.

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2. Catalysts (Cont'd.)

Particle size: It is of interest to note that the change in catalyst particle size had considerable effect on the results. Towards the end, I.G. used sizes between 0.5 and 1.0 mm. This led to increased output from the unit catalyst volume. It was concluded that the inside of the particles did not participate in catalysing the reaction.

The drop in catalyst size from 1-2 mm. to 0.5-1 mm. made it possible to lower the temperature from 198° to 191° C. This in turn increased the ratio of $H_2O : CO_2$ in the reaction products, since the shift decreases at lower temperature.

Synthesis in "fluid bed" reactors and fluid bed reduction tests had been scheduled but were never started.

3. Synthesis - Operating Conditions. (See ref. II/1 to II/13 at end of this section).

(a) CO_2 Formation.

The CO and H_2 are consumed in the synol synthesis in the ratio of 1.1:1.0 ($CO:H_2$) but regular watergas ($CO:H_2$ = 1.0:1.1) may be used for the synthesis. The catalyst is susceptible to sulphur poisoning and requires a feed gas as equally pure as the FT plants. A maximum of 25% inerts in the gas was acceptable.

It was stated that the synthesis should be carried out at the lowest temperature possible.

It was found practical to use the formation of CO_2 as controlling variable for the maximum production of alcohols. The less the conversion proceeds in one stage, the less CO_2 formed and the more alcohols recovered. 10% is considered the maximum value for the volume % of CO_2 in the exit gas from the synthesis. The CO_2 may be scrubbed out before entering the next stage or returning the gas to the reactor (recycle).

(b) Temperature.

Over a given catalyst and at a definite pressure and CO content of the feed, the temperature in the reactor is the means for control of the conversion one wishes to obtain. This temperature is between 190-195° C in the first stage and may exceed 210° C in the following stages depending on the inert content of the gas, particularly the CO_2 content. CO_2 in

3. Synthesis - Operating Condition (b)(Cont'd.)

quantities of 5-6% has a poisoning effect in that it requires a higher synthesis temperature and thus lowers the alcohol yield.

Towards the end of the war the German government lost interest in the synol development and insisted on directing the research toward production of fuels. I.G. then planned to continue with the installation of the synol plant, but operate under conditions which would give little alcohol and mostly olefines ("Benzinfahrweise"). This could be done very simply by raising the temperature of the synthesis. The operation at 260-300°C over the same catalyst produced a gasoline of 40-60% olefines with 65-75 octane number (res.). This operation was admittedly a means to continue work on the project and is not considered an improvement over the synol operation.

In order to illustrate the difference in the two methods, the following data are listed below giving results from two types of operation:

Both columns refer to the identical fuzed iron catalyst:

Type of Operation	Synol	Gasoline
Pressure	25 atm.	25 atm. maximum
Temperature	190-225°	210-245°
Feed Gas	Watergas	S free
Yield gm/m^3 CO+H_2	150 gm liquid 50 gm gasol	140 gm liquid 14 gm gasol
Stages	4	3
Space velocity V/H/V	150	250
Specific output tons/m^3 catalyst/day	0.60	0.92
Catalyst life	9 months	6 months
Product Distribution:		
Gasoline - 200° C	44-60%	40-70%
"Diesel" 200-300° C	18-15%	30-15%
Gasoil 300-400° C	15-10%	30-15%
400° C	23-15%	-

The alcohol and olefine content of the various fractions from Synol are as follows:

Fraction	Alcohol	Olefine	Paraffin and Rest
200° C	40-50%	45-30%	5-30%
200-300° C	56%	20-30%	14-24%
300-400° C	50-60%	15-25%	15-35%
400° C	10-30%	45-30%	25-60%

3. Synthesis - Operating Condition (b)(Cont'd.)

Note: Between 200-400° the "Rest" varies from 3-8%.

In general the increase in temperature lowers the alcohol and increases the olefine yield. As the catalyst ages, it slowly loses its activity and requires increasingly higher temperature. Thus the alcohol yield decreases over the life of the catalyst.

The same general rules, applicable in FT operation apply equally in synol: more alkali in the catalyst, lower temperatures, lower space velocity (within limits) give higher boiling products. There were however, indications that the desirable middle fraction could be increased individually by using precipitated instead of fused catalyst of identical composition. The reasons for this were not recognized.

(c) Pressure.

The preferred pressure range for the synol synthesis is 18-30 atm. (25 at optimum). At higher pressure the Fe-carbonyl formation is substantial. At the same time it becomes more difficult to remove the heat of reaction and this in turn leads to carbon deposition on the catalyst. The alcohol/olefine ratio is little affected by pressure.

(d) Recycle.

The "Kreislauf" operation described in Section I(a) of this report may be used equally well in synol operation. It is simply necessary to remove substantially all water from the reaction product before returning the gas to the oven. This drying tends to suppress the CO_2 formation sufficiently to obtain 90-93% conversion (on a gas containing 6% inerts) without intermediate scrubbing of the CO_2. The removal of CO_2 particularly by way of the alkalized-type processes is not easy in this case due to the fatty acids formed in the synthesis.

It was also found that the life of the catalyst was dependent on the partial pressure of the water in the reactor. In a "Kreislauf" run when the water was removed from the reaction products before recycling, and using 2500 V/H/V total gas load, the catalyst ran 7 months without losing its activity. This compares in the once through (3-stage) operation with a maximum of 3-4 months catalyst life.

Another beneficiary effect of the "Kreislauf" is of course the immediate removal of the synthesis products from the reactor. Thus any

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3. Synthesis - Operating Condition (d)(Cont'd.)

secondary dehydration or hydrogenation is suppressed. The higher alcohols in the C14 - C17 range are particularly affected by this operation. Due to the increased gas volume, these products are swept out of the reactor as vapors. In the once through operation they condense on and are decomposed by long contact with the catalyst.

Using recycle space velocities of 2000-3000 V/H/V (based on total feed) allows 90 - 94% conversion in two stages only (while 4 are required in the once through operation). Under these conditions 1 mol. CO_2 is then formed from 12 mol. feed gas.

Some operating figures may illustrage the Kreislauf operation:

The data are based on a fresh feed gas of the following composition:

CO plus H_2	86.0%
CO_2	5.5%
CH_4	5.0%
N_2	3.5%

Change of recycle gas composition with conversion (1 stage only).

% CO plus H_2 converted	Kreislauf composition CO plus H_2	CO_2	CH_4	N_2
90%	25.7	44	19.6	10.6
85%	35	38	17.5	9.5
80%	42	33.5	15.8	8.7
65%	62.5	17.3	12.9	7.3

These figures are all based on the same catalyst volume. Thus to obtain higher conversion at lower CO - H_2 content the synthesis temperature must be raised; this in turn increases the CO_2 production (the conversion to CH_4 was assumed as 8% in all cases).

Operation in liquid phase was not considered applicable for synol because long contact on the catalyst is characteristic for this technique. However, the use of "Kreislauf" may make liquid phase operation feasible. I.G. had proposed to study this process but the end of the war prevented further work).

4. Equipment.

The inclined synol reactor has been described in detail in the preceding Section I(b). It is in principle a reactor using a flat catalyst

4. Equipment (Cont'd.)

bed. The cooling tubes were embedded in the catalyst and were designed as bayonet tubes with one end closed. This arrangement was chosen to facilitate filling and removal of the fine grained catalyst.

For a further development the Germans had designed a twin oven consisting of a common centerpiece which carried 2 inclined cooling coils within the catalyst. Each bed was to contain 6 m^3 of catalyst.

There had been several different pilot plant ovens used in the laboratories including 2 vertical tube-reactors with the catalyst inside the tubes. (Tube diameter 15 and 20 mm.) At the same time a horizontal plate reactor (inside a pressure drum) was also installed. This unit is practically identical with the Lurgi design. Only one short run was made with this oven.

In order to protect the catalyst in case of a failure in the cooling system hydrogen was admitted and all CO purged from the catalyst as fast as possible.

The catalyst apparently forms a solid mass at the end of the run and must be drilled out of the tubes (80 working hours to empty 1300- 15 mm. tubes). Before the catalyst can be removed it is first extracted with an intermediate fraction of the product (150 - 240° C) by passing the liquid through the tubes for 1/2 hour. It is then dried and deactivated with N_2.

The unloading procedure in the case of the plate reactor was still more complicated.

The new design (inclined tube handle) had not been tested in any large scale pilot unit, but the I.G. engineers had great hopes that it would solve all problems. All other equipment used in the pilot plant such as blowers, CO_2 washers, coolers, charcoal adsorbers were conventional.

5. Products from Synol Operation. (see reference II/14 to II/18 at end of this section).

(a) Alcohols.

It has been stated that the main objective of the synol process was the production of straight chain terminal alcohols of boiling range as high as C_{20}. Thus a new class of chemicals had been developed from a

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laboratory curiosity to a commercial product. It has already been described how this objective could be reached, but the inventors themselves could not give an exact answer why it was possible to do it by way of the process described.

One German expert offered the explanation that alcohols are the primary products when the synthesis is carried out at low temperatures. They are dehydrated to olefines in a second step. This assumption may find some basis in the fact that the sum total of alcohol plus olefine in synol operation is fairly constant over a wide temperature range.

The products leaving the reactor are recovered in an oil and water phase, the water containing up to 25% organic compounds. These compounds include low boiling alcohols, ketones, aldehydes, acids and esters, and some salts of short-chained fatty acids. The oil phase contains enough high boiling products to solidify at room temperature. The methods used to separate the products are given in a later section.

The constitution of the products has been studied in great detail. The **alcohols**, up to C9 are practically straight chain primary alcohols. No secondary alcohols can be found. The same is substantially true of the higher alcohols (methanol and ethyl alcohol are produced only in traces).

(b) Olefines.

The olefines are mostly α-olefines. A C_{12} olefine was analyzed and found to have 60% of the double bond in α-position, while the rest was distributed with decreasing percentage toward the middle of the molecule. It was concluded that primarily all olefines are terminal, but due to isomerization the double bond is moved towards the middle of the molecule. Iron carbonyl is believed to catalyze this shift. A similar effect was observed in the oxo-synthesis where the presence of cobaltcarbonyl causes a shift of the double bond.

The sum of alcohols plus olefines in the product is between 70 - 80%, the alcohol ranging around 60% and over.

(c) Esters.

Esters are always present in certain fractions. That arsenic in the catalyst increases ester production up to 25% has already been stated. The ester content generally increases with the boiling range. Esters make

5. Products from Synol Operation (c)(Cont'd.)

up as much as 10% in the C_{10} alcohol range and increase to 20% in the C_{18} range.

The formation of the ester (and acid) has been explained by the direct reaction of CH2 radicals with CO and water. In the preparation of fatty acids from alcohols and CO, the following chain of reactions is assumed to take place:

(1) Decomposition of the alcohol to free radical and water

$$CH3\ OH \longrightarrow CH2 = H2O$$

(2) Reaction of radical and CO to form ketene

$$CH_2 = + CO \longrightarrow H_2\ C = CO$$

(3) Ketene may react with water or excess alcohol to form the corresponding acid or ester:

$$(a)\ H_2C = CO + H_2O \longrightarrow CH_3\ C\ O\ O\ H$$

$$(b)\ H_2C = CO + CH_3OH \longrightarrow CH_3\ COOH_3$$

The free radical is of course extremely short lived and present in only small concentration. It is therefore necessary to operate with high CO concentration to have the necessary acceptor ready to react with CH_2 the moment it forms. This explains the high CO and low alcohol concentration required for this process. The theory may be applied to FT or synol syntheses and offers a good explanation for the high acid and ester yield. The presence of CH_2 radicals in the hydrogenation of CO is generally acknowledged and with CO and H_2O (or alcohol) also present, the synthesis to acid and ester could follow the chain of reactions described above.

(d) Aldehydes and Ketones.

Aldehydes and ketones are both found in the product. The lower aldehydes can be extracted with bisulfite solution. The ketones are more stable and give no trouble. During the separation of the alcohols with boric acid they remain in the neutral oil. The lower ketones (acetone) are found mostly in the aqueous phase. There are some other classes of oxygenated compounds found in the primary product such as esters and unsaturated ethers, but they rarely make up more than 1% of the total. The products recovered and isolated so far are mostly the alcohols from C_1 to C_{22}.

5. Products from Synol Operation (d)(Cont'd.)

The products obtained from synol operation according to "Benzin-Fahrweise" resemble those contained in FT synthesis over Fe catalyst.

The gasolines from synol must be refined before they can be used as motor fuel. They are unstable and corrosive and do not have a sufficiently high octane number (see reference II/17 at the end of this section).

A raw gasoline had the following properties:

Distillation	IBP	35° C
	50%	108° C
	90%	148° C
	EP	200° C
Gum (after 7 days)		202 mg.
Cu strip		colors gasoline blue
OH number		191
Octane No. (res.)		54.0

The gasoline was refined over Fullers earth at 300° C., using 0.5 - 1 volume liqu./hr/volume Fuller's earth. The resulting product was as follows:

Distillation	1 BP	34° C
	50%	90° C
	90%	180° C
	EP	198° C
Gum (after two days)		0.5 mg.
Cu strip		Negative
OH number		6.5
Octane No. (res.)		72.5

The treatment consists essentially in dehydration of the alcohols to olefines and condensation of the aldehydes to high boiling polymers which are fractionated out.

The losses depend of course on the alcohol content and thus on the temperature of the synol operation itself. The increase in ON is substantial, but I.G. had still further considered the use of olefine isomerization to shift the terminal double bond towards the middle of the molecule as an additional means to improve the knockrating.

The diesel oils obtained in this operation do not compare with those from cobalt catalyst FT plants. 62 Cetane number was given as an average value.

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6. Uses for Synol Products.

This problem was of great interest since some of the products are a new commodity on the chemical market. Of greatest importance appear the alcohols. The C7 - C11 range may be esterified with acids of equal chain length (produced from the same alcohols) and used as plasticizers. The C9 - C14 fraction can be used for esterification with adipic acid to produce outstanding lubricants. This is an important use. The lower alcohols $C_3 - C_8$ may also be used for esterification to yield lacquer solvents. The synol alcohols are preferred on account of their straight chain character.

However, the most important application (in Germany) would have been the use of the higher alcohols in the detergent field. Due to their straight chain structure synol alcohols resemble the natural fatty alcohols. From them they differ only by way of their content of even and uneven numbered carbon atoms. The uses for the corresponding olefines are well known, with polymerization to synthetic lube oil in first place and sulphonation for the production of emulsifiers and detergents as an alternative. This entire field is presently in a state of development.

7. Separation of Products.

The separation of the various products has been the subject of considerable work by I.G.

(a) Pretreatment.

Before the alcohols, olefines and the neutral oil can be separated, it is necessary to take certain steps regarding the undesirable by-products. As such, are classified the acids and their reaction product with alcohols, the esters. Other undesirable compounds are the aldehydes and ketones which appear in only small quantities.

The acids must be neutralized with alkali to prevent further alcohol losses to esterification. A simple caustic wash is sufficient for this purpose. If it is also desired to de-esterify the product, the caustic wash may at first be omitted.

The esters are preferably saponified with strong alkali at 130° C. A 30 minutes treatment with good agitation is sufficient. The alcohols are thereby set free and the acid neutralized by the alkali. At the same time the reactive aldehydes are condensed to form heavy polymers and thus wind up in the high boiling fraction (see on the next page).

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7. Separation of Products (a)(Cont'd.)

If the esters are not removed, they appear in the following fractionation according to their boiling range and thus induce alcohols and acids into these fraction where they do not belong.

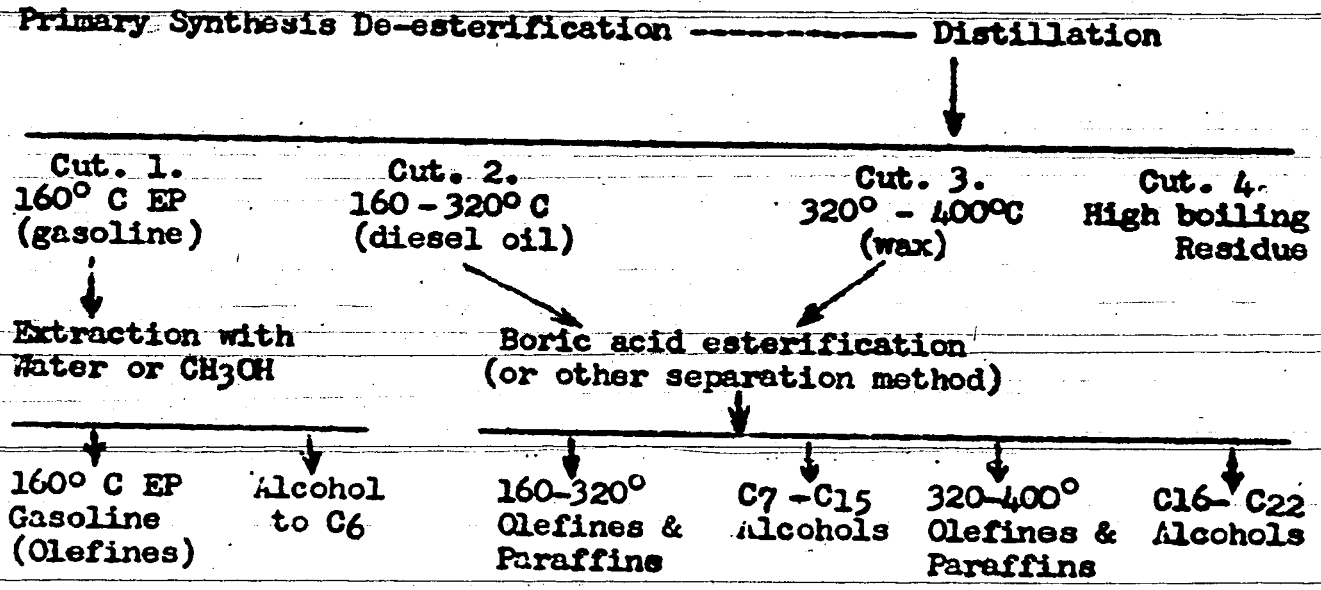
(b) Fractionation. (See reference II/21 at end of this section).

A sharp fractionation of the raw product is apparently essential for the exact separation into alcohols and hydrocarbons. This is particularly the case when boric acid-esterification is used as a means of separation.

The lower alcohols (to C_3) are practically completely dissolved in the aqueous phase of the product. The C_4 to C_6 alcohols may be washed out with water or possible methanol-water solution. This water wash is automatically carried out when the product is first de-esterified since the alkali must be washed out with water.

The higher alcohols may be seperated and prepared in 95 - 97% purity, provided the original feed is fractionated sharply. Several methods were studied by the Germans.

A simplified flowchart of a synol process may look as follows:



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7. Separation of Products (Cont'd.)

(c) Boric Process. (See reference II/22 at end of this section).

Boric acid esters are used for the separation of higher synol alcohols from the accompanying olefines and neutral oil. It is essential that the feed to the esterification unit be fractionated as sharp as possible. 50° C boiling range appears to be satisfactory for each cut.

One of the difficulties which require further work is the distillation of the neutral oil from the boric acid ester. The mixture must be thoroughly agitated. At the same time a temperature in excess of 250°C must be avoided in any step of the process.

The highest alcohol produced to date by this method is $C_{22}H_{45}OH$. Higher alcohols cannot be separated from the oil without decomposition.

The principle of the process is based on the fact that

(a) The alcohols esterify readily with boric acid at elevated temperature.

(b) The esters are considerably higher boiling than the alcohols (and accompanying compounds).

(c) The esters are easily hydrolyzed with water and the alcohols recovered.

In the process of this type the boric acid used for esterification must be substantially pure B_2O_3. But at the same time only a dilute solution of B_2O_3 is obtained in hydrolyzing the ester. This operation is expensive since large quantitites of solution must be concentrated.

It was found however, that a saturated aqueous solution of boric acid could be used in the hydrolysis step. This solution could be separated from the free alcohol by settling, and upon cooling, the additional free acid would precipitate from the solution. The acid crystals could be recovered by filtration and used immediately for further esterification. The process is applicable to all types of alcohols and in particular for the oxo process.

The esterification yields a certain quantity of water which must be removed. This is done by extractive distillation with benzine. The esterification requiros elevated temperature, and thus the water and benzene are simply carried overhead as they form.

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7. Separation of Products (c)(Cont'd.)

Following the removal of the water, the neutral oil is distilled to leave pure ester in the kettle of the column. The ester is then hydrolyzed with hot aqueous boric acid solution.

Below find operating data for one example:

The raw material from the synthesis has the following composition:

Alcohols	50% vol.
Olefines	40% "
Paraffins	9% "
Acid, Ketones etc.	1% "
	100% "

This mixture was fractionated to give the following cuts:

(1)	0-100° C	30% vol.
(2)	100-200° C	20% "
(3)	200-300° C	16% "
(4)	300-400° C	17% "
(5)	400° C +	17% "
		100% "

The object was to recover the alcohols boiling between 200° and 400° C. For this purpose fraction 3 and 4 were treated separately.

Treatment of fraction 4:
Feed: 100 kg. of fraction containing 72% wt. alcohol.
6.6 kg. boric acid.
575 kg. benzene

The mixture is agitated and heated to 90° C for 2 hours.

575 kg. benzene }
4.8 kg. water } distilled overhead

Distillation is then continued under vacuum.

The neutral hydrocarbons distill overhead. A total of 28 kg. is recovered in the receiver.

The kettle product, i.e., the boric acid ester after is transferred to the saponifier, where it is treated at 95° C for 30 minutes with 55.5 kg. of a 2.6% aqueous boric acid solution. The free acid solution is then allowed to settle at 95° C and is withdrawn. The solution now containing

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7. Separation of Products (c)(Cont'd.)

10.9% wt. (i.e., 38.8% saturation at 95° C) is next cooled to 2° C. The excess boric acid crystallizes and is centrifuged. 5.2 kg. boric acid are thus recovered. The filtrate, 50.5 kg., is returned to the system.

The free alcohols, 72 kg., are also withdrawn from the saponifier. 1.5 kg. boric acid still remain in solution. For its removal the alcohols are washed with 56.2 kg. water. The alcohol passes 3 counter current wash stages.

(d) Separation by Silicagel Adsorption. (see ref. II/25 at end of this section).

This method was considered by the Germans at one time for the separation of synol alcohols and deserves to be mentioned here.

The method is based on the difference between the heat of adsorption between alcohols and hydrocarbons.

	Heat of Adsorption		
methanol	15.0	Cal/gm	Silicagel
ethanol	14.8	"	"
n-butanol	13.0	"	"
n-octanol	12.0	"	"
n-decylalcohol	12.7	"	"
n-hexane	5.3	"	"
n-dodecane	6.1	"	"
water	16.1	"	"

The mixture is contacted with the dry gel and then washed with a volatile low boiling hydrocarbon solvent (petrol ether). The hydrocarbons are thereby removed. The alcohols remain adsorbed and may then be removed by such polar solvents as lower boiling alcohols or ketones and ethers. The gel is finally regenerated.

The gel may be loaded according to its quality, the particle size (1-2 mm) and the alcohol boiling range. For 170-180° alcohols, 15 g/100 g gel may be reached.

The adsorption must be carried out at room temperature or even below. The alcohol should be desorbed as soon as possible. The regeneration of the gel may be carried out with hot gases (N_2, CO_2) at 150° C and 1 : 1000 V/H/V.

(e) **Separation of Azeotropic Distillation.** (see ref. II/24 at end of this section).

Glycols are known to form azeotrope mixtures with many classes of organic compounds. In the case of synol products it was found that glycols may be used for separation because:

(1) Their azeotropes with hydrocarbons boil considerably below their azeotropes with equally high boiling alcohols.

(2) The azeotrope with hydrocarbons contains considerably more hydrocarbons than one with the alcohols.

(3) The glycols and the hydrocarbons in the overhead separate into two phases in most cases.

(4) The alcohols which are carried over the top remain dissolved in the glycol phase and may thus be easily returned to the column.

Particularly suited are of course those glycols which form azeotropes with hydrocarbons only and not with the alcohols. Butanediol 1-3 and hexane-diol 1-6 fall in this category.

Another particular advantage of these compounds is their high efficiency, i.e., the low volume ratio between the azeotropic carrier and the overhead component. This ratio may further be lowered by operation under vacuum. The following figures may serve as an example:

Using butanediol 1-3 on a 230 - 245° fraction the ratio of glycol to hydrocarbon is 2:1 at 1 atm., but only 1:1 at 20 mm. Hg.

In selecting the third component it is desirable to have the initial boiling point of the mixture 10-20° C above the boiling point of the carrier. The other oxygenated compounds such as ketones and esters are usually distilled overhead with the hydrocarbon.

It is possible first to enrich the mixtures of synol products in alcohol content by selective extraction with methanol. Thus 80% alcohols may be obtained in the mixture. 100 pts. of such a mixture (230-270° C) are distilled with 10 parts butanediol 1-3 at 20 mm. Hg. to give an alcohol concentration in the kettle as high as 98%.

The process is generally limited to alcohols from C_8 on up.

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7. Separation of Products (Cont'd.)

(f) Separation by Extraction with Aqueous Methanol. (See ref. II/23 at the end of this section).

The process is based on the higher solubility of the alcohols in the methanol solution. The necessary quantities to reach an alcohol concentration of 97% are given below.

Synol Fraction	Alcohol Content	CH_3OH Conc'n used	Vol. CH_3OH Solution for 1 vol. synol	% Alcohol in the neutral oil.	% Non-alcohol in the Alcohol
120-170° C	56	68	2	0.1	3.0
170-220° C	48	76	3	0.3	3.0
220-270° C	40	81	6	0.6	3.5
270-320° C	29	85	10	1.0	3.5

For practical purposed the extraction method is limited to C_{12} alcohols maximum.

The methanol is separated from the extract by distillation. Upon removal of the CH_3OH, the higher alcohols and the water separate into two phases and the water is withdrawn.

The methanol extraction or enrichment may be of interest in combination with the use of glycol to obtain final alcohol concentration (see above)

(g) High Boiling Products.

It was pointed out that prior to separating the alcohols from the neutral oil, the raw synol product had to be fractionated. The fraction boiling above 400° C was not considered in the process. Alcohols above C_{22} cannot be prepared by the boric acid method as the neutral oils cannot be removed from the ester by distillation.

The high boiling product is dark brown, probably due to Fe which is contained in quantities up to 0.1% (due to ironcarbonyl). The product may be used as such for certain industrial purposes. It can be treated with Fullers earth to give slightly yellow waxes. Pour points are usually varied from 70 to 105° C. The high ester content of these products makes them more ductile than FT wax. If necessary they may be hydrogenated to give high melting point waxes of the FT type.

8. Conclusion.

The synol process may be considered the most important development in the field of $CO-H_2$ synthesis carried out in Germany during the war. It is a means to synthesize in one operation a valuable chemical, such as high boiling alcohols.

The process appears to be entirely practical and requires no extreme operating conditions or expensive catalysts. It is the first achievement in the general trend to direct Fischer-Tropsch type synthesis away from fuels and hydrocarbons and towards especially defined compounds. It seems likely that the synol process, with certain variations could be changed to produce oxygenated compounds, such as esters and acids.

9. List of References.

There are appended to this Section II the following German documents:

1. "KW Synthese aus CO and H_2 Stand am 1. August 1942" - by Wintzer, Reisinger, Breywisch.
2. Verfahren zur Herstellung von Sauerstoffhaltigen Verbindungen - Patent Dept. Leuna, 23 September 1942.
3. Herstellung von sauerstoffhaltigen Verbindungen - I.G. Farben patent application, 15 October 1943.
4. Verfahren zur Herstellung von O_2-haltigen Verbindungen - Kreislauf Verfahren - 8 March 1943.
5. Verfahren zure katalystischen Reduktion von CO und H_2 - I.G. patent application, 23 June 1943.
6. Synolsynthese - by Breywsich April 1943 - Referat Merseburg #10
7. Die Synolsynthese - by Reisinger, February 1943 - Austausch der THK.
8. Bericht #472 by Breywisch, 10 October 1944 - Erfahrungen mit den halbtechnischen Synolanlagen Me 458.
9. Bericht #283 by Reisinger, 2 May 1941 - Bericht ueber Synol Synthese.
10. Bericht #326 by Wenzel : 10 April 1942 - Stand des Synolproblems.
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14. One drwg. M:4342-1 24 July 1941 - Schema fuer die Destillation der Synolanlage Leuna.
15. One drwg. M-4375-1 - Schema fuer die Syntheseanlage d. Synolanlage Leuna.

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9. List of References (Cont'd.)

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18. Gesetzmaessigkeit bei d. Dehydratisierung hoeherer Alkohole - by Asinger, 9 April 1943.
19. Zusaetzliche Esteroel-Alkohole - 9 July 1942 by Pohl.
20. Aktennotiz re: Nachbehandlung von Synolprodukt fuer Motortrebstoffe, 9 January 1942.
21. One drwg. Fliess-und Mengenschema fuer Verarbeitung der Synolprodukte, M-9802-2
22. Verfahren zur Abtrennung von Alkoholen aus nichtwaesserigen Fluessigkeiten. 7 April 1941.
23. Abtrennung aliph. Alkohole d. Estraktion mit waesserigen Methanol - by Menzel, 22 November 1944.
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25. Abtrennung von Alkoholen aus Gemischen mit Kohlenwasserstoffen - by Geiseler, April 1943.
26. Verfahren zur Reducktion eisenhaltiger Katilisatoren - patent application, 7 July 1941.
27. Roentgenfotografische Analyse von Kontakten - 2 July 1941.
28. One drwg. M-6459-4 - Schema der Kontaktreduktion.
29. Reduktion von Eisenschmelzkontakt - 15 July 1943.
30. Erweiterung und Verbesserung der Reduktion von Kontakt fuer Synol - 6 March 1943.
31. Mechanismus der Bildung von Fettsaeure aus CO und Alkohol - by Dr. O. Fuchs - 4 May 1936.

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SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

SECTION III

SYNTHESIS OF HIGH MELTING POINT WAXES

SUMMARY

The attached report covers laboratory work carried out by Kaiser-Wilhelm-Institut on the synthesis of high boiling waxes over Ruthenium catalyst. The results have been published in 1940 - 1941. They are mainly of theoretical interest.

Content.

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THE SYNTHESIS OF HIGH MELTING POINT WAXES

1. General Introduction.

The use of Ruthenium as a catalyst for the production of high M.P. wax from CO and H_2 was published in 1941 in "Breunnstoff Chemie". 19.22 P.226, the monthly magazine published by Kaiser Wilhelm Institut at Muehlheim. Copies of this paper are available in the United States for ready reference. The information obtained on the subject is briefly given in this report.

The process is mostly of theoretical interest and was not carried out beyond the laboratory stage.

A patent application was filed on May 1938 disclosing the use of Ruthenium (and/or catalysts containing Ru) at temperatures from 150 to 280° C and pressures above 30 atm. for the production of solid aliphatic hydrocarbons from CO and H_2.

2. Catalyst.

The catalyst is prepared by melting Ruthenium with KNO_3 and KOH to give potassium ruthenate which is dissolved in water and boiled under addition of methylalcohol. RuO_2 is precipitated, filtered, washed, and dried. The oxide is reduced with synthesis gas ($CO:H_2 = 1:2$) at 150° C and atmospheric pressure.

The catalyst may however be prepared by different methods. The essential requirement is that Ruthenium be present in as great dispersion as possible. Carriers, such as Kieselguhr may be used, but they have apparently no effect on the synthesis.

3. Operating Conditions.

The yield in hard wax increases with pressure and decreases with temperature. Optimum conditions seem to be 195° C at 150 atm. pressure.

Space velocities from 1-2 liter gas/hr/gm Ru are used. The yields given by KWI are 150-160 g/m^3 ideal feed gas.

The catalyst is quite susceptible to poisoning by sulphur, but with a pure feed gas, its life is exceedingly long. A two year run was made with one charge without any catalyst regeneration.

3. Operating Conditions (Cont'd.)

It should be noted that I.G. Leuna tried to duplicate the results without success. They obtained a brown product containing only 40% hard wax. The catalyst furthermore lost its activity within a few days. It appears that sulphur containing gas may have been used.

4. The Products.

The product is a wide mixture of high boiling waxes. The paraffins are mostly exclusively straight chain hydrocarbons with only a small percent of tertiary carbon atoms.

The waxes were separated by known methods such as extraction at increasing temperatures and different solvents.

Individual waxes with molecular weights of 10,000 were found having a melting point of around 140° C. This seems to be the maximum melting point. Increased mol. weight does not further influence the melting point.

5. Reference.

The following German document is available at the library of the Bureau of Ships in Washington, D.C.

1. Patent application by KWI dated 7 May 1938.
   "Verfahren zur Herstellung von festen aliphatischen Kohlenwasserstoffen".

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THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

SECTION IV

SUMMARY

The attached report covers the development of the isosynthesis by "Kaiser Wilhelm Institut" of Muelheim. The process includes the synthesis of low boiling isoparaffins (particularly isobutane) from CO and H_2 over thoria catalyst at pressures between 200 and 1000 atmospheres.

All work connected with this process was carried out in laboratory scale only.

ISOSYNTHESIS

Content.

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ISOSYNTHESIS

1. General Introduction. (See also ref. IV/1 and IV/2 at the end of this section)

The synthesis of low boiling isoparaffins was discovered in the laboratories of the Kaiser Wilhelm Institut at Muelheim. The discovery was made accidentally, when various oxides were studied for their use as catalysts in the synthesis of aromatics. It was observed that thorium oxide gave a high percentage of iso paraffins.

The process is a variation of the methanol or rather isobutyl synthesis. It operates at temperatures above those used in methanol synthesis, although CH_3OH is believed to be an intermediate product. The temperature range for the synthesis is limited on the one hand by the decomposition of CO (carbon deposit) at roughly 550° C. This limit is constant for all pressures. The lower temperature limit on the other hand is a function of the operating pressure. At 1000 atmospheres the isosynthesis may be carried out at 400° C. At 100 atmospheres a minimum of 450° C is required. More detailed information is presented in the following paragraphs.

2. Chemistry of Synthesis.

The Kinetics of the Synthesis is assumed to be as follows:

(1) Formation of Methanol from CO and H_2.

(2) Dehydration of alcohol and immediate reaction with additional CO and H_2 to isobutylene and higher isoparaffins.

(3) Polymerization of isobutylene possibly followed by hydrogenation of alkylate, or formation of dimethylether from methanol through addition of CO and H_2.

At very high pressure the reaction proceeds in the following direction:

$$CH_3OH + CO + 2H_2 \longrightarrow CH_3OCH_3 + H_2O$$

The dehydration of the methanol is an important step and operation at temperatures above those favoring methanol formation are specified.

Isobutane is one of the main products but the reaction is necessarily not as clear cut as presented above. It is also noteworthy that a small fraction of naphthenes and aromatics is usually found in the products.

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2. Chemistry of the Synthesis. (Cont'd.)

The theory is in good agreement with the fact that the addition of dehydration catalyst to the thorium oxide has a beneficiary effect on the yield.

3. The Catalysts.

It was pointed out that the catalyst used initially was pure ThO_2. Some 10% alcohols (mostly water soluble) are obtained with thorium alone. The addition of aluminum (or other dehydrating catalysts) yields a product almost free of oxygenated compounds.

(a) Thorium Catalyst.

Basic thorium carbonate is precipated with soda from thorium nitrate solution and the precipitate washed free of alkali. Even small traces of alkali lower the catalyst activity and require higher synthesis temperatures. The filtered thorium carbonate is dried at 110° C, pelleted, and finally treated at 300-400° C with air passing through for 1 to 2 hours (no reduction is necessary).

The thoria catalysts are outstanding in their insensitivity to suphur poisoning. Treatment with H_2S or CS_2 does not effect the activity; even the use of $(NH_4)_2S$ for precipitation of the thoria gives normal conversion.

The long life of this catalyst is remarkable. It may be used several months without sign of aging. Even in case of carbon deposits and the resulting increase in pressure drop through the bed, the original activity can be restored by passing air over the catalyst at synthesis temperature.

The results obtained on pure thoria catalyst are given in the section on operation.

(b) Mixed Catalyst.

The high price of thoria and possibly its lack in Germany led to attempts to use substitutes and it was found that most dehydrating catalysts such as oxides of aluminum, sirconium, tungsten, or rare earths can be used provided that sufficiently high pressures are applied. On 2 October 1943, a patent application was filed disclosing the use of these substances either alone or in a mixture of thoria.

2. Chemistry of the Synthesis (Cont'd.)

It is claimed that these dehydrating substances direct the synthesis towards oxygenated compounds below a certain temperature. Beyond this limit, however, isoparaffins are the main product. In addition to the dehydrating components it was found that substances which catalyze the formation of CH_3OH at temperatures below those of the isosynthesis are successfully used as additinal components in the catalyst. Zinc oxide is particularly named. It is, however, necessary that the dehydrating component be present in excess over the methanol forming part.

The preferred catalyst giving the best results according to the present day development is a thoria-alumina two component catalyst.

Thorium carbonate and alumina are precipitated separately. The precipitates are washed, mixed and dried at 300° C. Dilute solution gives less dense catalysts. The apparent density of pure thoria catalyst is 1.6- 1.8 (with concentrated solution 2.4 can be reached). The percentage of alumina based on thoria varies from 30- 40%. Contents under 20% show no effect. Above 40% CH_4 formation becomes excessive.

The alumina-zinc oxide (1:1) catalyst does not give comparable yields, only 100 gm/m^3 feed are recovered, compared to 130 gm/m^3 feed with thoria-alumina. It is, however, possible to use a two stage operation and thus obtain almost the same result with the cheaper catalyst.

4. Operating Conditions. (see also ref. IV/3 and IV/4 at the end of this section).

The CO and H_2 are consumed approximately in the ratio $CO:H_2$-1:1.2 with most of the oxygen being removed as CO_2. The CO_2 content in the exit gas is approximately 30%.

The synthesis is carried out in a once through operation (no "Kreislauf") with the feed gas containing $CO-H_2$ in the ratio they are consumed.

70-75% Conversion is obtained at average space velocities of 1350 V/H/V (10 times higher than in ordinary F.T. operation). The tests were carried out in 15 mm. and 25 mm. tubes of chrome nickel steel or copperclad steel.

500 lit/hr. was the maximum feed used in the laboratory to date. For larger scale operation the use of superheated steam or molten salt was considered as a cooling medium.

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4. Operating Conditions (Cont'd.)

(a) Influence of Temperatures.

The following table is based on operation at 1300 V/H/V and 150 atm. pressure; pure thoria catalyst.

	Product Distribution			
Temperature ° C	400°	425°	450°	475°
C_1 and C_2	4%	8%	13%	20%
C_3 and C_4	5%	9%	16%	29%
Iso C_4	11%	20%	28%	32%
Liquid Isoparaffins	55%	42%	23%	8%
Naphthenes	15%	15%	14%	5%
Aromatics	-	2%	4%	6%
Alcohols (oxygenated Comp.)	10%	4%	-	-
	100	100	100	100

With increasing temperature the spectrum moves toward lower boiling products, while the oxygenated products disappear to be largely replaced by aromatic compounds.

The reaction is not very sensitive to temperature change, ± 10° C are acceptable variations.

(b) Influence of Pressure.

The following table is based on operation at 450° C and 1300 V/H/V in a copperclad tube over pure thoria catalyst.

Yields are expressed in gm/m^3 ideal gas:

Pressure atmospheres	0	6	30	150	300	500
C_3 and n-C_4	-	-	5.1	9.1	20.4	16.0
Iso C_4	-	-	5.4	30.0	41.6	46.5
Gasoline and oil	-	Trace	16.1	29.7	37.4	40.5
		Trace	26.6	68.8	99.4	103.0

Use of chrome nickel tubes gave somewhat higher yields. The increased pressure and the correspondingly longer contact time increased the CO conversion. At the same time this increased conversion is not endangered

4. Operating Conditions (b)(Cont'd.)

by carbon decomposition which is less (at a given temperature) at increased pressure.

There is a slight carbon deposition in the course of the synthesis which makes it necessary to burn off the carbon from the catalyst. This is done every 3 - 4 weeks with air or air-recycle gas mixture at the synthesis temperature.

5. Products.

The synthesis products obtained with this process are mostly low boiling isoparaffins with isobutane the largest individual component.

Based on operation at 150 to 450° C, 1300 V/H/V, and pure thoria catalyst the following product was obtained:
(Note: This is same test shown in the first table under 450° C temperature).

Composition of "gasol":

C_3	20%
i C_4	70%
n C_4	10%
	100%

(No butylene was found)

Composition of liquid Product:

Fraction (°C)	Component	% of Liquid
20 - 33°	Isopentane	11.8%
33 - 47.8°	n-Pentane	1.0
	Neohexane	0.2
	Undetermined	0.3
47.8 - 64°	Neohexane	13.6
	Undetermined	1.7
64.0 - 88.5°	Naphthene	2.9
	* Paraffin	9.6
88.5 - 98.0°	1,3 Dimethylcyclopentane	9.4
	Isoheptane	5.1

* Probably contains 2, 4 dimethylpentane.

(Cont'd.)

4. Operating Condition (b)(Cont'd.)

Composition of liquid Product: (Cont'd.)

Fraction (°C)	Component	% of Liquid
98.0 - 113.0°	Naphthene	7.8
	Paraffin	3.7
113.0 - 131.3°	Naphthene	7.7
	Paraffin	2.4
131.3 - 239°	Naphthene and Aromatic	22.3
	Paraffin	-
239° +	Solid residue	0.5
		100.0% of vol.

The Octane Number (motor method) of the gasoline fraction varies from 79 - 85 clear.

6. Conclusions.

The isosynthesis is of technical interest as a directed reaction of CO and H_2. By the use of particular catalysts and operating conditions, CO and H_2 can be combined to yield a hydrocarbon mixture consisting predominantly of isoparaffins.

The high temperatures and high pressure required for this synthesis would be a debit to its commercial use. As a fuel, the isosynthesis product would be of premium quality, but the components are otherwise of no special interest today.

7. List of References.

(1) Patent application by KWI dated 18 December 1942.
"Verfahren zur Kataytischen Syntheses von Kohlenwasserstoffen aus CO und H_2".

(2) Protocol of meeting, KWI and RCH, 2 June 1943.

(3) Progress report on development of Synthesis from CO and H_2 particularly synthesis of iso paraffins, by KWI, December 1942.

(4) Patent application by KWI dated 2 October 1943.
"Verfahren zure Herstellung von klopffesten Kohlenwasserstoffen".

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THE SYNTHESIS OF HYDROCARBONS AND CHEMICALS FROM CO AND H_2

SECTION V

ISOBUTANOL SYNTHESIS

SUMMARY

The attached report covers information regarding the synthesis of isobutanol and higher alcohols by a modified h.p. methanol process.

The isobutanol synthesis was a prewar I.G. development and was practiced extensively for the production of isobutylenepolymer (appanol) and iso-octane. The high boiling fractions, while only a small percentage of the total product were of great interest for the production of detergents and lube oil esters.

1. Isobutanol Synthesis.

The following information on the synthesis of isobutanol was obtained from Dr. Goggel of the I.G. Farbenindustrie at the Ludwigshafen plant on 28 May 1943. This synthesis is in essence an extension of the high pressure methanol synthesis which utilizes carbon monoxide and hydrogen. The isobutanol synthesis uses the same raw materials, practically the same catalyst, and pressures of the same magnitude (about 240 atmospheres). The catalyst used for the higher alcohols in zinc and chromium oxides with the addition of one percent of potassium hydroxide. The temperature used is about 430° Centigrade.

The main difference compared to the methanol synthesis is the lower output per catalyst volume, since the main product (CH_3OH) is recycled to extinction. Based on a once-through operation, the product made in greatest quantity in this synthesis is methanol; about five to six parts of methanol are obtained for every part of isobutanol. In addition to this, there are a great many other alcohols and ketones produced. The total weight of these products equals the weight of isobutanol in the product.

On a water free basis the total product contains approximately:

Isobutanol	14%
Methanol	63%

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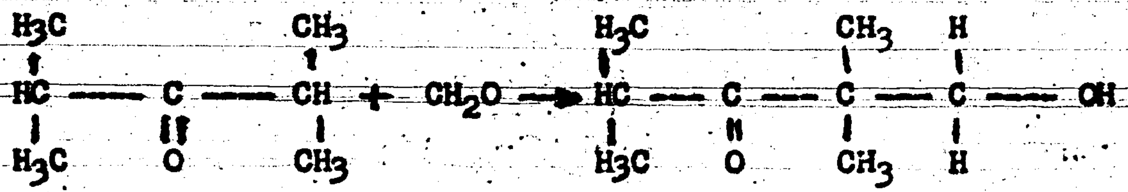
1. Isobutanol Synthesis (Cont'd.)

High alcohols and Ketones	15%
Hydrocarbons	5%

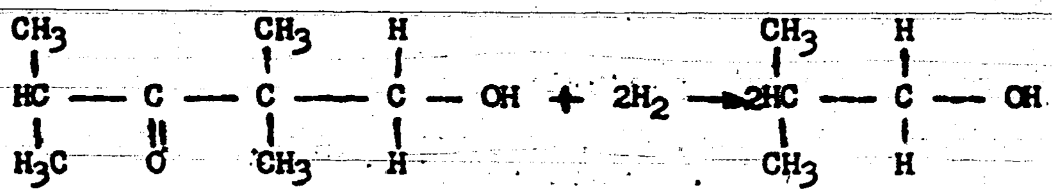
An important part of the isobutanol synthesis which increases the yield of isobutanol and utilizes one of the by-products is the reaction of "isobutyron" with formaldehyde to give 2 molecules of isobutanol. The "isobutyron" is apparently a misnomer and should more properly be called diisopropyl ketone. This reaction is as follows:

(a)



$$(H_3C)_2HC-\underset{O}{\overset{\|}{C}}-CH(CH_3)_2 + CH_2O \rightarrow (H_3C)_2HC-\underset{O}{\overset{\|}{C}}-C(CH_3)_2-CH_2-OH$$

(b)



$$(CH_3)(H_3C)HC-\underset{O}{\overset{\|}{C}}-C(CH_3)_2-CH_2-OH + 2H_2 \rightarrow 2(CH_3)_2HC-CH_2-OH$$

(See also reference V/6 at the end of this section).

The separation of the products from this synthesis is by fractional distallation. The equipment involved is not novel in any of its features but is complex only because of the multi-component mixture which must be separated. The distallation scheme is straight forward, using continuous flow through columns which remove one component at a time. (see ref. V/1 to V/5 at the end of this report).

2. Details.

In the isobutanol synthesis a feed gas of approximately the following composition is used:

Carbon monoxide	32%
Hydrogen	57%
Nitrogen	Balance

2. Details (Cont'd.)

The catalyst is a pelleted catalyst with no binder, composed of the following:

Zinc oxide	60 parts
Chromium oxide	40 parts
Potassium hydroxide	1 part

The zinc oxide is broken up and chromic acid is added. The mixture is worked 1/4 hour, then 0.5% graphite is added as lubricant. The mixture is then moistened with distilled water (100 kg. ZnO, 60 Kg. Cr_2O_3, 20 lit. H_2O). A reaction occurs in 1/4 hour. The catalyst is then pressed into pellets 5-5 mm. 1% KOH is added to the final catalyst in form of fine K_2CO_3 powder. This is the only difference between isobutyl and methanol catalyst. The catalyst is charged to the chamber and reduced in the place. The conditions for the reaction are:

Pressure	240 atmospheres
Temperature	430° Centigrade

The composition of the gas leaving the converter is approximately as follows:

Carbon monoxide	22%
Carbon dioxide	5-6%
Hydrogen	57%
Nitrogen	5%
Hydrocarbons (mostly CH_4)	Balance

The analysis of the liquid product is approximately as follows:

Isobutanol	12%
Methanol	55%
Water	18-20%
High alcohols and Ketones	10%
Hydrocarbons	Balance

All methanol is recycled to the chamber. It is impure and purification cannot be economically justified. The recycle has no effect on the isobutanol yield. The methanol in the feed is considered simply like $CO + 2H_2$. A detailed listing of the compounds contained in the product is given here to illustrate the complexity of the composition. These are taken from the attached chart.

(a) Hydrocarbons, total about 5 per cent

Propylene
Propylcyclohexane

Diisobutylene
Triisobutylene

2. Details (Cont'd.)

(b) Alcohols - total about 70- 75%

Methanol
Ethanol
n-amylalcohol
Ethylisopropylcarbinol
Dimethylcyclohexanol
Propanol
Butanol
Isobutanol
Diisopropylcarbinol
Sec.-butylcarbinol

Aldehydes - total about one per cent

Formaldehyde
Isobutyraldehyde
Diethylacetaldehyde

Ketones - total about 8 - 10%

Acetone
Methylethylketone
Methylpropylketone
Ethylisopropylketone
"Isobutyron" (Diisopropylketone)
etc.

The balance if made up of acids, alctones, and phenols.

The condensation of "isobutyron" with formaldehyde is as follows; The materials are utilized in these ratios:

Material	Mols.
500 tons per month of 90% Isobutyron	3.95
500 tons per month of 30% Formalin	5.00
130 tons per month of 20% Sodium Hydroxide	0.65
500 tons per month of methanol (Solvent)	

These are charged batchwise to agitated autoclaves in such a manner that the sodium hydroxide catalyst is added over a period of 9 hours, while the temperature is maintained at 50° C. At the end of this period the crude condensation product is charged to a still in which the methanol is removed. The residue product from this distillation is washed with water to remove salts and the remaining formaldehyde, and is neutralized by the addition of sodium sulphide The washed crude product is then distilled to separate the unreacted "isobutyron" from the condensation methylol-isbutyron.