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REPORT I - INSPECTION OF FISCHER-TROPSCH PLANT

REPORT II - SEPARATION OF COKE-OVEN GAS INTO ITS CONSTITUENTS BY PARTIAL LIQUEFACTION

REPORT III - THERMAL CRACKING OR REFORMING OF COKE-OVEN GAS AT NORMAL PRESSURE

PLANT OF KLOCKNERWERKE, A.G., CASTROP-RAUXEL, GERMANY

Reported by

Capt. C. C. Hall, U.K.
Dr. A. R. Powell, U.S.A.

June 22, 1945

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(A Subcommittee of the Technical Committee)

of the

PETROLEUM INDUSTRY WAR COUNCIL

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PLANT OF KLOCKNERWERKE, A.G.

CASTROP-RAUXEL, GERMANY

Reported by

Capt. C. C. Hall, on behalf of British Ministry of Fuel and Power

Dr. A. R. Powell, on behalf of U.S. Technical Industrial Intelligence Committee.

CIOS TARGET NO. 30/5.03

Fuels and Lubricants

22 June 1945

COMBINED INTELLIGENCE OBJECTIVES SUBCOMMITTEE
G-2 Division, SHAEF (Rear) APO 413

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Capt. C. C. Hall, British Ministry of Fuel and Power
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A. R. Powell, U. S. Petroleum Administration for War

REPORT I -- INSPECTION OF FISCHER-TROPSCH PLANT

Personnel making inspection:

Capt. R. A. A. Taylor, Br. (CAFT)
Capt. C. C. Hall, Br.

Date of Inspection: April 12th and 14th, 1945

General:

The site at Castrop-Rauxel includes two distinct sections: (1) a colliery with coke-ovens and by-product plant, (2) a synthetic ammonia plant including plant for the liquefaction of coke oven gas and separation into its constituents, and the Fischer-Tropsch plant. With the exception of the colliery, all plants were in a badly damaged condition.

No inspection of section (1) was carried out, and in the synthetic nitrogen part of the works only the liquefaction of coke-oven gas was dealt with. The information obtained on the latter process is covered in a separate report.

Personnel Interviewed:

Dr. Volmer, chemist, Assistant to Director Alberts, who was not present, but was available at his home "An der Muhle", Waltrop, and was later interviewed in connection with target 30/5.01, Ruhrchemie, A.G.

Dr. Braune, manager of the Fischer-Tropsch plant.

Description of Plant and Process

The Fischer-Tropsch plant was completed in 1936 and then had a daily output of 50 tons liquid products. By 1938 this had been increased to 100 tons. During the war years the output has averaged 100-110 tons liquid products together with 15-17 tons gasol per day (i.e. ca. 40,000 tons primary products per annum).

Production and Purification of Synthesis Gas

Water gas is produced in 4 Damag sets (150,000 m^3/day/set) with two old Pintsch generators as stand-by. The 600,000 m^3 of water gas is blended with 300,000 m^3 of synthesis gas per day. Details, including drawings, for the coke-oven cracking process were obtained by a separate team of investigators and are recorded in a separate report. The composition of the gases is available in the laboratory records which were obtained.

The mixed gas contains 3-5 gm. H_2S/m^3 which is reduced to 4-5 gm./100 m^3 in Klönne towers containing luxmasse. The organic sulphur, 15-20 gm./100 m^3, is reduced to 0.5-0.6 gm/100 m^3 by passing through the usual luxmasse-sodium carbonate mixture at 150°-250°C., contained in 4 parallel sets of two towers each, 3 sets on stream and one stand-by. The synthesis gas is heated in preheaters fired with F. T. residual gas, and there are exchangers between the first and second tower of each set. Each set of two towers contains 60 tons of mass and after this has handled 38-40,000 m^3/hr. for about 6 weeks, tower No.2 becomes No. 1 and the original No. 1 is recharged. The system then runs for a further 6 weeks, i.e. one charge of mass remains on stream for 12 weeks.

Before entering the purification stream, 0.25 percent of pure oxygen (obtained from the Claude unit supplying nitrogen for ammonia synthesis) is added to the gas. This has the effect of converting the sulphur in the feinreinigung process to sodium sulphate and the mass continues to function as long as any free sodium carbonate is left.

The gas leaves the normal feinreinigung system at a temperature of 150°C. and is then passed through one large tower containing 132 tons of organic sulphur removal contact. This tower reduces the sulphur to 0.1-0.2 gm./100 m^3 and lasts for 2 years without recharging.

The Synthesis

The contact-oven house contains 63 normal-pressure Mannesmanne tube-and-plate ovens arranged in two rows "back-to-back". In the normal arrangement, as at Sterkrade-Holten, the two rows of ovens face inwards with a central control gallery where all steam-drums, gauges and controls are located. The Castrop arrangement necessitates two control galleries, one on each side of the oven house.

Of the total number of ovens 53-55 are on stream at one time, approx. 33 on Stage 1 and remainder on Stage 2. Each oven contains 3 tons of catalyst of composition, Co 30 percent, ThO_2, 1.5 percent, MgO 2.5 percent, balance - kieselguhr, obtained from Ruhrchemie.

Stage 1 receives the input of 900,000 m^3 of syngas per day; the gas contraction is about 50 percent, and the temperature regulated to maintain this contraction. The outgoing gases from Stage 1 pass through both direct condensers and active carbon absorbers before entering Stage 2. The overall gas contraction is 75 percent.

A freshly-charged oven is placed on Stage 2 at about 185°C. It remains there for 30-35 days during which time the temperature may have reached 192°C. It is then solvent extracted and placed on Stage 1 at about 185°C. and runs for about 3 weeks when a temperature of 190°-191°C. will have been reached. It is then treated with solvent and subsequently at 14-day intervals. It remains on this stage for 120 days before the catalyst is discharged and returned to RCH for regeneration. The life of an oven filling is thus 150-160 days.

During the last working year (1944), immediately following the 5th or 6th washing and when the catalyst had reached the stage when it would normally have been discharged, the catalyst was treated with pure H_2 at 200°C. for 8 hours at 1500 m^3/oven/hour. The subsequent synthesis temperature was found to be only 176°-177°C. to obtain the normal activity. However, after only 20 days' synthesis the plant was put out of action by bombing and the test could not be completed. The plant personnel were convinced that by using this combination of solvent and hydrogen treatment the ultimate life of the catalyst would be well over 200 days. The procedure was first tried by von Löpmann of Kemen-Dortmund.

The solvent extraction process consists in allowing 28 m^3 of F.T. benzin to trickle down over the catalyst during a period of 7 hours.

Condensation

The direct-condensation towers are packed with stoneware rings and are fed with water which is recycled via a cooling tower. The C_1-C_4 acids dissolve in the water and the acid water is replaced with fresh to the extent necessary to maintain not more than the equivalent of 1 gm. acetic acid per

litre. The C_5-C_{15} acids remain dissolved in the oil condensate.

The active carbon system for each stage comprises 8 towers, those on Stage 1 outlet containing 9 tons carbon a piece, those on Stage 2 outlet, 7 tons.

Products

The average working yield of C_3 + higher hydrocarbons varies between 135 and 150 gm./Nm^3 ideal gas. The composition is as follows:

Benzin - 160°C.	:	50 percent
Diesel oil, 160°-230°C.	:	20 "
Heavy oil, 230°-320°C.	:	20 "
Gatsch, over 320°C.	:	10 "

Gasol (65 percent C_3 (25% olefines); 35 " C_4 (75% ")) 15% of total products.

Methane: 14-15 percent of total products.

The amount of residual gas available is 200,000 m^3/day and is used for fuel as follows:

Power station	:	50,000 m^3/day
Small C.O.G. cracker	:	25,000 "
Large " "	:	50,000 "
Feinreinigung	:	35,000 "
Distillation	:	15-20,000"
Heating coke ovens	:	remainder

Treatment of Products

The condensed oil and A-K benzin are washed with alkali and fractionated in a 25-plate column. The benzin cut is stabilized at 15 ats. and the gasol sold as motor fuel in bottles and tank cars. The benzin, O.N. 47-53 (I.G. Research) is sold for blending. Since 1942 or 1943 only the light cut 160°-230°C. d_{20} 0.755 has been sold as a diesel oil component and the remainder of the normal diesel oil cut, the 230°-320° portion, sent to I.G. Merseburg for sulpho-chlorination to produce the "Mersol" detergents. The gatsch went to Witten for soap manufacture.

The benzin used for catalyst extraction is distilled separately and the recovered hard wax (m.p. 90°, 1-1/2 tons/oven filling or ca. 3 percent of total products) sold as such.

A polymer gasoline plant built in 1942 to process 25 tons gasol/day at 200 ats. by the I.G. phosphoric acid process had only been run experimentally for 10 days. A 45 percent weight yield of polymer gasoline was expected.

A "Carbulol" cracking plant had been in use up to 1939.

Continuous Production of Synthesis Gas Under Pressure

Some years before the war a plant had been built for the cracking of F. T. residual gas with oxygen and steam at 10 atmos. pressure. The plant (which still existed) comprised 4 towers connected in series, A and D being (originally) CO_2 scrubbers, B and E the cracking chambers, together with a combined saturator-cooler. Trials were made with coke-oven gas and it was found that the reaction $CO_2 + CH_4 \text{ ---- } 2CO + 2H_2$ proceeded and that CO_2 removal was unnecessary. Towers A and D were therefore filled with chequer brick and used as preheaters. The flow was alternately, A ---- B ---- C ---- D, D ---- C ---- B ---- A. The functions of B and C were, alternately, cracking at 1100°C. and "burning" with oxygen at 1180°-1350°C.

The treatment of residual gas was only tried out for a few days in 1937 and later experiments have been carried out with coke-oven gas. In all these, the dome of the combustion tower fused after a few days' operation, despite care and the addition of steam in the introduction of the oxygen.

The trouble was believed to be due to the maximum temperature being attained above the path of the main gas stream through the tower, and the heat consequently becoming too intense at the dome. The oxygen inlets were therefore placed lower down the tower and also increased in number. The onset of the war, however, stopped further experiments and the new arrangement has not been tried out.

The plant was built to treat 1000-1200 m^3 of gas/hr. and the idea was to use tail gas from medium-pressure synthesis to produce gas for medium-pressure synthesis and to avoid thereby a large part of the compression costs.

The effect of pressure is to retard the formation of carbon black and laboratory experiments had shown that this was entirely suppressed at 10 atmos.

Using residual gas, the CO_2 can be adjusted to the requirements of the reaction by pre-washing.

It was stated that owing to the "mechanical" difficulties the results obtained during the trials are not of much value, but the methane content was apparently reduced to 5 percent in the cracked gas.

C. C. HALL

REPORT II -- SEPARATION OF COKE-OVEN GAS INTO ITS CONSTITUENTS BY PARTIAL LIQUEFACTION

Personnel Making Inspection:

E. L. Baldeschwieler, U.S.
Ernest Cotton, U.S.
A. R. Powell, U.S.

Date of Inspection: April 13, 1945

Purpose of Inspection:

Although the primary purpose in listing this plant at Castrop-Rauxel as a target for C.I.O.S. inspection had been the fact that a Fischer-Tropsch plant for the manufacture of synthetic oil was located there, it was considered advisable to obtain also some information on the unit for separation of coke-oven gas into hydrogen, ethylene, etc., since such an operation might, under some conditions, be used to produce such gases for the manufacture of synthetic oil or related products.

Personnel Interrogated:

Two employees were interrogated, Dr. Weinhoff, an engineer quite familiar with this particular plant operation, and Dr. Vollmer, a chemist.

Description of Plant:

The separation plant consisted of five units: four Claude units, each with a capacity of 8,000 m^3 of coke-oven gas per hour, and one Messer unit, with a capacity of 10,000 m^3 of coke-oven gas per hour. The operation of a Claude unit is essentially as follows:

The coke-oven gas is compressed to 25 atmospheres by four stages of compression with inter-cooling between each stage. The gas is then washed with water at a rate of 100 m^3 of water per hour per unit, which removes most of the carbon dioxide and residual hydrogen sulphide in the gas. To ensure substantially complete removal of these acid constituents, the

gas is then subjected to a second wash, this time with 10 m^3 per hour of a 3% solution of ammonia. This ammonia solution is continuously regenerated for cyclic use by flowing through a stripping tower where the carbon dioxide and hydrogen sulphide are released by heating with indirect steam.

The gas is then subjected to progressive refrigeration in three towers as follows:

First column operating at -110°C. removes the so-called ethylene cut as a liquid, which contains approximately 35% ethylene, 15% ethane, and 50% methane (molol percentages).

Second column operating at -180°C. removes the methane cut as a liquid.

Third column operating at -220°C. is the hydrogen purification column. Here the carbon monoxide is removed from the gaseous hydrogen by down-flowing liquid nitrogen. This liquid nitrogen comes from an air separation plant located near the gas-separation units, and the total liquid nitrogen required for reduction of carbon monoxide to a very low percentage is about 1000 m^3 (gas volume basis) per hour for all five units.

The liquid nitrogen, containing carbon monoxide, issuing from the third column was, after vaporization, added to the coke-oven underfiring gas.

Following the hydrogen purification column, the gaseous hydrogen is expanded through a reciprocating expansion engine lubricated with liquid nitrogen, and is thereby cooled to a very low temperature. The expanded highly cooled gaseous hydrogen, as well as the vaporized and expanded liquid cuts, serve as refrigerants for the process, as is universal practice for all gas liquefaction schemes.

The purified hydrogen was considered the chief product of this separation plant. It was used in the ammonia synthesis plant, and was never used in the Fischer-Tropsch unit. The methane cut, after vaporization, was run back to the coke oven for underfiring fuel. It was planned to further purify the ethylene cut for recovery of relatively pure ethylene, and for this purpose a Linde gas separation unit was installed. This operated for about six months and was then destroyed by bombing. Dr. Weinhoff disclaimed any knowledge of the ultimate use of ethylene other than that it was to be shipped to another company.

The Messer unit was not described in detail, but Dr. Weinhoff stated that it was practically identical to a standard Linde unit. He claimed that operation of the Claude units was less expensive than that of the Messer unit.

Dr. Weinhoff stated that total cooling water required for the synthetic ammonia plant (producing 180 metric tons ammonia per day) was 1500 m^3 per hour, and that about half of this water was required for operation of the coke-oven gas separation plant. Power requirement for both the Claude units and the Messer unit was approximately 300 kw. hr. per 1000 m^3 of coke-oven gas.

Dr. Weinhoff was asked about the problem of nitric oxide in the coke-oven gas, since this impurity, present in extremely small amount, had been known to cause bad explosions in gas separation plants. He said this was completely removed by adding 0.5% oxygen to the gas and passing it through a holder kept at 95°C. During the delay period in the holder, the nitric oxide was completely removed.

Conclusions:

There appear to be no features of this gas separation plant that were not previously rather well known. However, a flow diagram of the Claude unit was procured from Dr. Vollmer and was sent to London along with other C.I.O.S. documents for further study.

A. R. POWELL

REPORT III -- THERMAL CRACKING OR REFORMING OF COKE-OVEN GAS AT NORMAL PRESSURE

Personnel Making Inspection:

E. L. Baldeschwieler, U.S.
Ernest Cotton, U.S.
A. R. Powell, U.S.
Captain R. A. A. Taylor, Br. (CAFT)

Date of Inspection: April 13, 1945

Purpose of Inspection:

The preparation of synthesis gas for the Fischer-Tropsch synthetic oil plant at Castrop-Rauxel included, not only the usual blue-water gas unit, using coke as the fuel, but also a large "Koksofengas Spaltun Anlage", or a plant for the thermal cracking of coke-oven gas in the presence of steam. By this process, most of the hydrocarbons in the coke-oven gas are converted into hydrogen and carbon monoxide. Since the original coke-oven gas contains about 50% hydrogen, the resultant cracked or reformed gas consists largely of hydrogen with a minor percentage of carbon monoxide. By mixing this high-hydrogen gas with water gas, the proper ratio of hydrogen to carbon monoxide may be obtained for Fischer-Tropsch synthesis gas with less conversion of the water gas by the shift catalyst. Since the coke-oven gas reforming unit is directly connected with production of Fischer-Tropsch synthetic oil, it was considered essential that data and information be obtained.

Personnel Interrogated:

Dr. Vollmer, a chemist, gave most of the information, and was assisted by Dr. Weinhoff, an engineer, for a rather brief inspection and oral interrogation.

Description of Plant:

The plant consisted essentially of four large steel towers, heavily lined with refractory brick and filled with refractory checker brick. In general, construction of these towers was not unlike the Cowper stoves used in conjunction with iron blast furnaces. It was understood that these four towers operated as two units with two towers running in series in each unit.

The total cycle of operation for each unit was 15 min. divided into the following periods:

7 minutes: Heating by combustion of tail gas (Restgas) from the Fischer-Tropsch plant, combustion gas being discarded through the stack.

1/4 minute: Coke-oven gas containing water vapor introduced, but outlet gas discarded as a purge operation.

7 minutes: Collection of the cracked or reformed make gas.

3/4 minute: Combustion again started but collection of outlet gas continued to recover make gas remaining in chambers. It was understood that the two units operated so that one unit was making reformed gas while the other was heating, so that gas make was substantially continuous from the plant as a whole.

The temperature maintained in the chambers was quite high, ranging from 1350° to 1400°C. Prior to entering the cracking chambers, the coke-oven gas passed through a tower where it was saturated with water vapor at 70°C., and this insured the presence of the proper percentage of water vapor for the reforming reaction.

The chief chemical reaction occurring in the cracking chamber is:

$$CH_4 + H_2O = 3H_2 + CO$$

The methane (CH_4) content of the original coke-oven gas was 22-25% and that of the reformed gas was 3-5%.

The volume of coke-oven gas cracked in this plant was 6,000 m^3 per hour, the heating value of this gas being 4,300 kg. cal. per m^3. The volume of Fischer-Tropsch tail gas used for heating was 2,000 m^3 per hour, the heating value of this gas being 2,500 kg. cal. per m^3.

Comments:

This plant had been designed by Klöcknerwerke engineers themselves, according to the personnel interrogated. It differs in some respects from the thermal gas cracking process of Heinrich Koppers, especially as regards means for heat economy, but the essentials of the process are much the same, and apparently the composition of the cracked gas produced is substantially the same as that obtained from the installation of Heinrich Koppers made at Rheinprussen Fischer-Tropsch plant at Homberg on the Rhine. Reference should therefore be made to the report on the Rheinprussen plant, as well as to the interrogation of Heinrich Koppers organization in Essen for related information.

The above covers only the high spots of the design and operation of this coke-oven gas cracking plant at Castrop-Rauxel as obtained from a very brief inspection and interrogation, and documents from the plant sent to C.I.O.S. in London will undoubtedly give more detailed information.

A. R. POWELL