

VI. Synthesis Plant

The general procedure involved in the Moers Fischer-Tropsch operations will be reviewed prior to consideration of the individual steps in greater detail.

Water gas is made from coke in eleven Koppers generators and is passed in part through a catalytic convertor unit to increase the ratio of hydrogen to carbon monoxide. Coke oven gas is "cracked" with steam non-catalytically in a battery of six Cowper stoves and is mixed with converted water gas in the proportion required to give a 2:1 ratio of hydrogen to CO. The mixed gas subjected to coarse purification (Grobreinigung) for H₂S removal by passage through iron oxide, and then is contacted with iron oxide plus sodium carbonate at elevated temperature for fine purification (Feinreinigung) to remove organic sulfur. The purified gas goes to the first stage of synthesis ovens, comprising two thirds of the total, and then to water scrubbers and charcoal absorbers for removal of condensable products (C₃ and heavier). The unabsorbed gases pass through the second stage of synthesis ovens and to a final water scrubbing and charcoal absorption. Oil condensate from the water scrubbers is fractionated to make several distillate cuts and waxy bottoms known as "gatsch". The light hydrocarbons recovered from the charcoal are stabilized to yield benzoin bottoms and a C₃-C₄ fraction overhead which is liquefied under pressure and designated by the somewhat confusing term "gasol".

A. Water Gas Generation

The water gas generators are arranged in two batteries. The older battery, containing six generators was built in 1936 and a second battery of four generators was built in 1938. A fifth generator was added to the latter battery in 1943. Fairly complete drawings and descriptions of these generators were picked up (Doc 25) which indicate that they were conventional in construction and operation except for somewhat more elaborate provisions for recovering waste heat than would be used in the United States. It was stated that normally nine of the eleven units were in service and that the total coke consumption was about 900 (metric) tons per day. The operating cycle of each generator was given as 80 seconds blast, 6 seconds purge, 60 seconds up run, 50 seconds down run, and 6 seconds purge.

From the data in a seized record book (Doc. 19), Table III, page 24, has been prepared summarizing the operation of these generators as carried out in 1941 and 1942.

The remains of the old battery of water gas generators is shown by Figure 13, page 25.

B. Water Gas Conversion.

Approximately 18% of the water gas produced was passed through a pair of catalytic converters to increase the ratio of H₂ to CO. The average performance of these converters is also shown in Table III. These converters are approximately 3 meters in diameter and 6 meters high, and operated at 450-500°C. The converted gas is water washed and combined with the remainder of the water gas in holder (55).

From seized document No. 61, it appears that the converter catalyst contained the following ingredients although its entire composition was not given:

Cr	3.7%
Mn	0.1%
P	0.1%
As	Trace

A sample stated to be fresh converter catalyst was obtained. The results of an analysis of this sample made by the Fuel Research Station are given on page 23a.

C. Coke Oven Gas Cracking.

To further increase the synthesis gas supply and to complete the adjustment of the H₂:CO ratio to the desired 2:1, coke oven gas in the amount of about 10,000 cubic meters per hour is "cracked" with steam in a battery of three Cowper stoves. These are refractory lined chambers approximately six meters in diameter and twenty meters high packed with refractory checker brick. No significant drawings or further details of construction were obtained. The stoves are used in rotation on a cycle comprising blast, steam purge, "crack", and steam purge. The cracking temperature was stated to be 1200°C. From seized document No. 19 the following figures were taken as representative of this cracking operation in 1941 and 1942.

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Water-gas Shift Catalyst, Sample No. 6.

This sample consisted of greyish-brown, irregular-shaped pieces, approximate size range, 1/2 to 3/4 in., of great hardness and mechanical strength. Bulk density: 1300 g./liter.

<u>Analysis:</u>	<u>%</u>
Moisture (by distillation with xylene)	5.0
Additional moisture given off at 800°C.	13.0
Si O ₂	5.1
Fe ₂ O ₃	38.5
Cr ₂ O ₃	5.4
Al ₂ O ₃	2.5
Ca O	18.2
Mg O	5.2
-CO ₂	5.0
-SO ₃	1.9
Difference (alkalies, etc.)	<u>0.2</u>
	<u>100.0</u>

This analysis presents no unusual features. Chromium oxide is a normal promotor for the shift catalyst, and lime is a recommended addition, burnt dolomite being often used as the basis of the catalyst.

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TABLE III.

OPERATION OF WATER GAS GENERATORS
AND CONVERTORS.

Average composition of coke.

H ₂ O	8.2%
Volatile + C	82.6%
Ash	9.2%

Average Generator Operation.

Coke charged to generators	981,220 metric tons/day.
Water gas produced	1,146,070 M ³ /day.
Gross steam consumption	= 1870 metric tons/day.
	= 95 pounds/Mcf.
Steam generated in waste heat boiler	= 1095 metric tons/day.
	= 56 pounds/Mcf.
Net steam consumption	39 pounds/Mcf.

Average Converter Operation.

Water gas converted	210,900 M ³ /day.
% of total water gas	18.4%
Converted gas volume	260,400 M ³ /day.
Steam consumption (30 atm)	86 metric tons/day.
Water consumption	1,004 M ³ /day.
Coke oven gas cracked	251,590 M ³ /day
Steam to cracking stoves	250.4 metric tons/day.
Cracked gas production	389,370 M ³ /day.
Coke oven gas used as fuel	4,862 M ³ /day.
Heating value	4,455 Cal/M ³ .
Other gas (Rest gas) used as fuel.	122,200 M ³ /day.
Heating value	2,292 Cal/M ³ .

D. Synthesis Gas Purification.

The mixture of converted water gas and cracked coke oven gas is passed at atmospheric temperature to a battery of eight "Grobreinigung" towers for removal of H₂S. Each tower is approximately 11 meters in diameter and 10 meters high, containing 800 tons of catalyst in beds about 0.3 meters deep on 18 trays spaced 1 meter apart. The catalyst is stated to be iron oxide (luxmasse) and to have a life of about 12 weeks after which it is thrown away. The gas velocity through the catalyst was stated to be 1 meter per second. Air in the amount of 1.4% of the gas treated is added to the gas ahead of the coarse purification to function as an oxidizing agent in the subsequent fine purification step.

A sample of this catalyst was obtained. Results of its analysis as reported by the Fuel Research Station are as follows:

Moisture	49.5
Loss on ignition at 475°C.	5.4%

The ignited and air dried catalyst showed the following analysis which is typical of Luxmasse:

Moisture	3.4%
Si O ₂	0.8
Fe ₂ O ₃	56.0
Al ₂ O ₃	27.4
CAO	6.2
SO ₃	1.9
CO ₂	2.2
Difference	<u>2.1</u>
	<u>100.0%</u>

The fine purification (Feinreinigung) plant for removal of organic sulfur comprises a battery of five chambers filled with lump catalyst containing iron oxide plus sodium carbonate. The chambers were 4.7 meters inside diameter and about 6 meters high with brick insulated walls to facilitate operation at elevated temperature. The gas is preheated in a small pipe heater to reaction temperature which ranges from 180°C with a fresh catalyst to 280°C when the catalyst is nearly exhausted.

A sample said to be the fine purification catalyst was obtained and identified as CIOS Sample No. 9. The result of the analysis of this sample as reported by the Fuel Research Station is as follows:

Moisture	8.0
Fe ₂ O ₃	34.4
Na ₂ CO ₃	23.8
SO ₃	3.5
Unidentified	30.3

Miscellaneous laboratory notes (Document 61) indicate that the fine purification catalyst contains about 29% of Na₂ CO₃. Apparently experiments on the regeneration of the fine purification catalyst with oxygen were conducted in 1941 from the records of which the following information was derived:

The fully spent mass showed as a typical analysis 33% Na₂ SO₄, 0.3% Na₂ SO₃, and 4% Na₂ CO₃. This indicates that the reaction in Feinreinigung is essentially a catalytic oxidation and that O₂ in the synthesis gas is essential, as other documents and data have indicated. Spent mass that had not been regenerated showed - 16 - 30% Na₂ SO₄, 0.4% Na₂ SO₃, and 7 - 15% Na₂ CO₃. The above analyses indicate that the original mass contained about 30% Na₂ CO₃, the remainder presumably being Fe₂ O₃.

The gas leaving the fine purification and going to the reactors was stated to have the following composition.

CH ₄	0.5%
Other hydrocarbons	0.2
CO ₂	8.0
O ₂	0.1
N ₂	8.0
CO	28.0
H ₂	55.0

From other sources it was learned that the sulfur content is 0.4 to 0.5 gms S per 100 M³ after normal fine purification.

E. Synthesis Catalyst

The Moers plant used a cobalt Catalyst but the persons interrogated claimed to know nothing more about its composition except that it had not changed since the plant started operations. The catalyst is obtained from Ruhrchemie at Oberhausen-Holtien and is returned to them for reworking. The catalyst is received in the reduced state in steel "Kubels" as illustrated by Fig 14. Each Kubel holds approximately 3 metric tons which is sometimes a little more and sometimes a little less than required to fill a single synthesis oven. An overhead travelling crane moves and dumps these containers. Return shipments of spent catalyst are made in the same Kubels which are carried on specially built rail cars holding two Kubels each.

One Kubel filled with what was stated to be fresh synthesis catalyst was found in the northeast corner of the synthesis building. The cover was not bolted tight and some deterioration of the catalyst might have occurred due to infiltration of air during several months standing. On 7 March the cover was partly removed and a small sample of catalyst taken (CIOS No. 10) without any special precautions to exclude air from the Kubel. The sample did not ignite spontaneously and the sample container was sealed promptly and the cover replaced on the Kubel. On the following day the cover was again partly removed to permit a large sample can to be lowered onto the top of the catalyst in the vessel. The can was previously purged with CO₂ and a blast of CO₂ was directed into the upper part of the Kubel while the sample was being taken. It was impossible to dig deeper than about one foot below the surface of the Catalyst and at this depth, where the sample was taken, the catalyst was observed to be at a dull red temperature.

Before removing the can of catalyst from the Jubel, the cover of the can was put in place and it was sealed with adhesive tape within a few minutes thereafter. This was identified as CIOS sample No. 2. The Fuel Research Station analyzed sample No. 2 and tested both samples for activity with the following results:

	%		%
Moisture	1.0	Ca O	0.9
Loss on ignition	4.0	Mg O	0.9 (0.9)
Si O ₂	47.9 (47.5)	Ni	0.1
Fe ₂ O ₃	6.5	-SO ₃	nil
Th O ₂	1.8 (1.8)	-CO ₂	0.2
Al ₂ O ₃	1.9	Unaccounted for	<u>5.6</u>
Co ₂ O ₃	29.2 (28.7)		<u>100.0</u>

The material "unaccounted for" may be undetermined elements or may be due to false assumptions as to the state in which the known elements are present in the sample.

The amount of material insoluble in acid 52.7% gives a minimum figure for the kieselguhr content, and 100 - (CO₂O₃+ThO₂+ MgO) gives a maximum figure.

The composition of the catalyst expressed in the usual manner would therefore appear to lie between the limits shown:

<u>Co</u>	<u>ThO₂</u>	<u>MgO</u>	<u>Kieselguhr</u>
100	8.8	4.4	260 to 330

This result is in complete disagreement with information obtained by the Ruhr Party, which was that the catalyst used in all Western-German Fischer-Tropsch plants had the composition:

100 Co, 5 ThO₂, 8 MgO, 180-220 Kieselguhr

The above analytical results should therefore be regarded as tentative.

Both samples 2 and 10, as obtained, were completely inactive for synthesis at 185°C. and 195°C. After reduction with hydrogen at 400°C. in the usual manner, both catalysts showed gas volume contractions of 10% and 20% respectively when evaluated at 185°C. and 195°C.

Although it is known that catalyst was not made or reworked by Rheinpreussen, no specific information has been found on the technology of these operations as carried out by Ruhrchemie and occasionally by Brabag. Some discussion of the subject took place in connection with controversy over the cost of reworking, included in Document No. 2 which remains to be studied in detail. From Document No. 7 recording shipments of catalyst from Ruhrchemie to Rheinpreussen Table IV, page 32 has been prepared. There seemed to be no significant trend in composition during 1942. Comparable figures for June and December 1943 and June 1944 indicate no trend during these years unless possibly toward a slightly higher ratio of Kieselguhr to cobalt.

The total shipments of cobalt by month from July 1940 to September 1944 shown in Table V, page 33. The shipments were low in August 1942, in May, June and July 1943, January and February 1944, and June 1944 and later. There is no indication for the reason for these depressions, but it is possible that they were associated with bombings of Ruhrchemie plants or their sources of supply. The shipment to Rheinpreussen in September indicates some optimism even at that date about resuming synthesis operations at Moers.

The exact basis of calculation catalyst reworking costs is not clear from first reading of the seized account books, but it appears that Rheinpreussen's monthly payments to Ruhrchemie amounted to 3.7 to 4.2 marks per kilo of cobalt returned by Ruhrchemie.

A Rheinpreussen memorandum 27 August 1942 describes a method reported by Hoesch-Benzin for evaluating synthesis catalysts, involving measurement of hydrogen and carbon monoxide adsorption separately at normal pressure and temperatures of 50, 100, 150 and 200°C. It is stated that adsorption increases with temperature over this range and that much more hydrogen than CO is adsorbed per gram of cobalt. From these adsorption curves, it is implied that some

measure of activity can be derived although just how this is done is not explained.

From the minutes of conferences of Ruhrchemie licensees, extending over the period from November 1936 to July 1939 (Document 93), the following additional information about catalysts and operating conditions was derived.

Effect of ThO₂ - Mg O ratios.

No final conclusions were reached at the meetings as to the exact effect of the Mg O content. In general, the trend of opinion indicated that a ratio of 1 Th O₂ to 1.6 Mg O gave satisfactory results and about as good a catalyst containing a higher proportion of Th O₂. Further increase in Mg O content was tried but the experiments had not run long enough to determine its effect.

Sulfur Removal.

The major item of interest found in the discussion of sulfur removal concerned the effect of oxygen in the operation of the Feinreinigung. With 0.012 vol. percent O₂ the H₂S removal was very poor. With 0.177 to 0.205 volume percent oxygen, good H₂S removal was secured except at extremely high rates of gas throughput. When the O₂ content was increased to 0.802 to 0.903 volume percent, the efficiency of H₂S removal was seriously decreased. Organic sulfur removal was not very effective with 0.012 volume percent oxygen but was effective with 0.177 to 0.443 volume percent. The best results were secured with 0.177 to 0.205 vol. percent oxygen.

Miscellaneous Items.

Other matters discussed at the meetings concerned general matters of plant operation such as emptying and reloading the convertors with catalyst, removal of paraffin, removal of carbon deposits, and regeneration with hydrogen or by washing with Fischer-Tropsch product.

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TABLE IV
Components of Synthesis Catalyst
Shipments from Ruhrchemie to Rheinpreussen *

Month 1942	Cobalt	Kilograms shipped			Component Ratios by weight.		
		Thorium	Kieselguhr	MgO.	Th/Co	Kies./Co.	MgO/Co
Jan.	19571	995	32045	1481	0.0508	1.637	0.0756
Feb.	20922	1061	36323	1538	0.0506	1.735	0.0734
Mar.	21278	1096	36418	1644	0.0513	1.710	0.0771
Apr.	21681	1129	36060	1732	0.0519	1.658	0.0796
May	21571	1125	37343	1573	0.0521	1.728	0.0728
June	24163	1241	40994	1715	0.0513	1.691	0.0708
July	19966	1018	33729	1381	0.0509	1.688	0.0692
Aug.	13692	711	24243	1010	0.0519	1.770	0.0736
Sept.	21655	1121	37126	1605	0.0517	1.713	0.0740
Oct.	21313	1067	37141	1650	0.0500	1.741	0.0773
Nov.	11769	586	20396	867	0.0497	1.730	0.0735
Dec.	17536	888	29634	1290	0.0505	1.688	0.0734
<hr/>							
1942							
Totals & Ave.	235117	12038	401452	17486	0.0512	1.706	0.0744
June 1943	9281	467	18947	713	0.0503	2.040	0.0768
Dec. 1943	18231	928	39012	1352	0.0508	2.139	0.0740
June 1944	10853	545	19529	806	0.0502	1.799	0.0742

* Data from CIOS Document No. 7

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TABLE V.
Catalyst shipments from Ruhrchemie
to Rheinpreussen
Expressed as kilograms of Cobalt.

	1940	1941	1942	1943	1944
Jan		22220	19571	17928	15240
Feb		20360	20922	17452	14353
Mar		22453	21278	19864	19008
Apr		21010	21681	17653	20590
May		22896	21571	24881*	19340
June		23323	24163	24356**	10853
July	20904	22819	19966	13117	3603
Aug	21117	21367	13692	16727	None reported
Sept	16894	25310	21655	16988	24258
Oct	22843	21030	21313	20510	No further
Nov	15286	22992	17536	18065	Shipments
Dec	<u>21129</u>	<u>22985</u>	<u>17928</u>	<u>18231</u>	
Total	118173	268765	241276	225772	127245

* Includes 17335 kg. from Brabag

** Includes 13567 kg. from Brabag

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F. Synthesis Ovens.

The contact oven house is shown by Fig. 15, which also shows the extensive damage done to the south end of this building by bombing. The ovens are arranged in two parallel rows along the length of this building. The first 36 ovens, in the south end of the building, were erected in 1936; the next 12 were erected in 1937, and the last 48 were erected in 1938.

Figure 16 shows the outer ends of three ovens viewed from the ground level. Below these ovens can be seen the catalyst discharge troughs, and in the center is a portable bucket elevator for dumping spent catalyst into kubels for return to Ruhrchemie.

The synthesis ovens themselves were of the rather well-known early Ruhrchemie type, designed for low pressure operation. One of these ovens which had been removed from the battery is shown in some detail by Figures 17 and 18. For some unknown reason, the water tube leaders had been cut off from this reactor, but this leaves the spacing of the tubes more apparent.

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Each reactor is approximately 1.5 meters wide 2.9 meters high and 5 meters long. The horizontal water cooling tubes extend lengthwise of the reactor. There are 11 tubes in each of the 29 horizontal rows, the tubes being approximately 2.5 cm outside diameter. Horizontal headers, spaced as indicated by the cut-off rows of tubes in Fig. 18, are connected at both ends of the reactor and their ends join vertical headers at each corner of the reactor as can be seen partially on the reactor at the left in Fig. 16. The vertical headers on the same side of each reactor have a connecting line at the bottom. The vertical headers at the inner end (nearest the center of the building) of each reactor are connected to a superimposed steam drum, wherein steam pressure, and thereby reactor temperature is controlled.

The more recent units were arranged with a steam drum for each reactor as shown in Fig. 19 whereas earlier units had two reactors connected to each drum as shown by Fig. 20. Several units of each type are shown by Figures 21 and 22.

The edges of the transverse cooling plates can be seen in Figs 17 and 18 although the spacing is so close that the individual plates can not be distinguished. These plates are approximately 1 cm face to face. The catalyst fills the space between the plates and around the tubes.

No detail drawings or descriptive matter relating to reactor construction were found among the seized documents. It is understood that the reactors were made by Mannesmannrohren Werke, Dusseldorf.

G. Synthesis Procedure

It is customary to operate 60 ovens in the first stage and 30 in the second stage, with the remaining 6 emptying and filling or out of service for repairs or catalyst washing. Synthesis gas is supplied to the first stage of ovens direct from the fine purification step at a temperature of 150-160°C and at a rate of 1000-1200 cubic meters per hour per oven. (This stated rate is higher than indicated by captured documents.) The effluent is subjected to water scrubbing and charcoal absorption after each stage although in early operations only water scrubbing was used after the first stage. The catalyst temperature

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was stated to be 195 to 200°C and the pressure not over 3000 mm. of water (4.25 psi). The pressure on the cooling water is increased from 2.5 to 9.0 atm. during the life of the catalyst. This corresponds to a range of water temperature from 139°C. to 180°C. which does not seem reasonable for the stated 5°C. rise in catalyst temperature. It seems probable that the latter figure is in error, but nothing bearing on this point has yet been found in the seized records.

From a plant record book (Doc. 19) and corresponding graphs, a rather detailed picture of the performance of the synthesis ovens during the last half of 1941 and the first half of 1942 can be obtained. During this period the synthesis gas charge rate averaged about 630 cu.m. per hour per oven. The charge rate was in general quite steady but on some days averaged as low as 520 M³ per hour, and on others as high as 740 M³ per hour. The product yield figures, for some unknown reason, showed much greater fluctuations from day to day with no apparent correlation with charge rate. The total liquid product, including "Gasol" (C₃ and C₄ hydrocarbons) averaged 150-155 grams per cubic meter, with a daily minimum of 135 gm/M³ and a maximum of 175 gms/M³. The yield of products heavier than the "Gasol" averaged about 135 gm/M³ with a minimum of 112 gm/M³ and a maximum of 155 gm/M³.

The performance of the individual stages is also illustrated by reported data for 1941 and 1942 from which Table VI page 46 has been compiled. These data are derived from independent analyses of material to and from each stage and obvious inconsistencies suggest that analytical errors, in some cases, were considerable. For the period in question the CO-conversion in the first stage averaged about 70%, and in the second stage about 65%. The efficiency of CO utilization measured by the proportion converted to useful products (C₃ and heavier) is generally considerably lower for the second stage, probably in part because of the greater dilution of gas processed in this stage. There is no apparent explanation for certain exceptions to this relationship (18 September in particular). The original data also include hydrogen balances for these operations.

Further data on synthesis oven performance are provided by a collection of data sheets (Doc. 73) for tests conducted in April, May and June 1943. The calculation procedure was as follows:

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TABLE VI

Conversion in Individual Stages
of Synthesis

	<u>FIRST STAGE</u>		<u>SECOND STAGE</u>		<u>OVERALL</u>	
	<u>% CO Conv.</u>	<u>CO Conv. Eff. Fac.*</u>	<u>% CO Conv.</u>	<u>CO Conv. Eff. Fac.*</u>	<u>% CO Conv.</u>	<u>CO Conv. Eff. Fac.*</u>
<u>1941</u>						
23 July	74.7	3.33	77.9	1.49	94.5	2.76
8 Aug.	76.8	5.63	61.0	1.99	90.5	3.70
19 Aug.	70.6	4.00	64.0	2.35	89.3	3.76
28 Aug.	72.8	4.51	64.3	0.89	90.3	3.08
18 Sept.	75.8	4.02	65.2	7.69	92.3	4.26
2 Oct.	74.8	4.58	61.0	1.62	90.1	3.61
21 Oct.	75.6	3.14	68.1	2.82	92.3	3.37
5 Nov.	77.7	3.95	62.9	3.80	91.7	4.50
18 Nov.	78.2	4.86	79.0	2.48	95.1	3.22
9 Dec.	74.4	5.20	68.4	2.44	91.9	4.38
29 Dec.	76.4	5.37	69.2	2.82	92.6	4.68
<u>1942</u>						
6 Jan.	77.1	4.35	66.7	1.70	92.4	3.74
31 Jan.	74.0	4.65	57.8	4.38	89.1	4.10
10 Feb.	75.4	6.26	60.8	1.88	90.4	4.80
25 Feb.	78.3	3.80	69.4	1.87	93.4	3.40

* CO Conversion Efficiency Factor

$$= \frac{\text{Vol CO Converted to C}_3 \text{ and heavier}}{\text{Vol CO Converted to CO}_2, \text{ CH}_4 \text{ \& C}_2\text{H}_2}$$

Not calculated or designated as such in the original data.

Calculation shows a total yield of liquid products + gasol of about 155g/m^3 of pure synthesis gas ($\text{H}_2 + \text{CO}$). One of the tests made in series on both stages showed a calculated yield of 175.0 g/m^3 .

The normal life of a charge of catalyst is about four months. Three or four times during this period the catalyst is dewaxed by washing for 12 to 15 hours at 160°C with synthetic benzin having a boiling range of about 140 to 180°C . Hydrogenation was originally used for this purpose, the hydrogen being made by the iron-steam reaction. It was stated that benzin washing has been used for the last two years, because it is much more "effective", but it seems probable that the reason for the change was the desire to recover the high melting point wax instead of largely destroying it by hydro-cracking on the catalyst. The benzin is distilled from the extract and the residual wax, known as "Hart Paraffin" is cast in pans to make cakes for shipment.

An informal report from the Rheinpreussen laboratory dated 15 March 1938, entitled "The Removal of Paraffin from Used Catalyst" describes a series of experiments directed toward the removal of paraffin from used Fischer-Tropsch catalyst by its heating with water and solutions of NaOH , Na_2CO_3 and Na H CO_3 . The conclusions reached are as follows: -

1. By heating Fischer catalyst with a 4-5% soda solution at atmospheric pressure a satisfactory removal of paraffin can be achieved. The removal amounts to 65-75%.
2. For effecting a sufficient removal of paraffin the mixture of catalyst and solution of soda must be heated to above 100°C . The melting point of the paraffin in the catalyst is so high that a temperature of $96-98^\circ\text{C}$ is inadequate.
3. Small grain sizes of the catalyst are more difficult to free of paraffin than the larger ones.
4. Silica converted to soluble form during the treatment is only slight.
5. For a clean paraffin separation 3 parts of soda solution to one part of catalyst is considered most favorable.

A report from Brabag (Ruhland) transmitted to Rheinpreussen by letter dated 21 March 1938 discusses the efficiency of hydrogenation as a means for regenerating spent Fischer-Tropsch catalyst. The author concludes that a hydrogenation step for said catalyst having a reduced activity in consequence of desposition of paraffin therein is effective in increasing the life-period of the catalyst. The recommended conditions of hydrogenation are temperatures of 200 to 225°C and a flow of hydrogen equivalent to 1000 m³ per hour per oven. Compared with the production of catalyst ovens that have operated without hydrogenation for over 2000 hours, hydrogenation can increase the production about 25%.

The following disadvantages however attend regeneration by hydrogenation:-

1. The paraffin is not completely removed from the catalyst.
2. By reason of catalytic cracking a part of the paraffin in the catalyst is decomposed and
3. Paraffin (wax) of new and particularly high molecular weight are formed.

The comment in the second paragraph of page 6 is interesting. It states as follows:

"The formation of methane during the hydrogenation of the catalyst is at present viewed as an index of progressive cracking of iso paraffins because methane is manifestly a reaction product of these iso paraffins."

Informal reports from Brabag dated 4 and 5 January, 1938 (Doc 92) discuss experimental work on the effect of impurities in synthesis gasol laboratory experiments showed some advantage for final purification with active charcoal but plant tests did not confirm this advantage, probably because of other uncontrolled factors. Active carbon gave a sulfur content of only 0.1 - 0.2 gm/100 m³ compared with 0.4 - 0.5 gm/100 m³ from normal fine purification.

The hydrocarbon content of the synthesis gas is ordinarily 0.1 - 0.2 gm/m³ before fine purification and 0.5 to 1.0 gm/m³ after fine purification indicating some synthesis reaction which is suspected of involving resin-forming hydrocarbons. The effect of such hydrocarbons in synthesis is not definitely known.

An oxygen content greater than 0.12% by volume in the synthesis gas is known to be quite detrimental to the catalyst. The air introduced for fine purification leaves 0.02% of O₂ in the synthesis gas, but its effect on the synthesis catalyst is unknown. Fresh catalysts blanketed with CO₂ may become red hot due to reaction with oxygen in the air during transfer to the ovens but this does not seem to impair catalyst activity or life.

Carbon dioxide has not been found to enter into the synthesis reaction. Its chief effect seems to be as a diluent, causing lower conversions as the CO₂ content is increased and the CO + H₂ content is decreased, increasing the ratio of H₂ to CO appears to promote the hydro-cracking of oil and wax on the catalyst.

Increasing the ratio of CO:H₂ in synthesis gas tends to make heavier as well as more saturated products. Initial operation of a catalyst with synthesis gas relatively rich in CO seems to cause some permanent damage since abnormally short life results from subsequent operation with normal gas. Commercial fine purification does not remove all of the impurities which harm the catalyst. A spent catalyst contains bound CO₂ equivalent to 7-8% of the cobalt when calculated as carbonate.

Thiophene and other cyclics seem to be the most detrimental type of sulfur compounds. A given amount of sulfur as thiophene is much more detrimental if benzol is also present. Pure benzol or naphthalene apparent does not harm the catalyst. Acetylene up to 1% in the synthesis gas does not appear harmful.

High space velocity, once through, gives reduced percent conversion but increased unit productivity. Recycling gives a lower boiling product and a recycle ratio of 2.5 to 1 gives practically no oil heavier than benzol. Decreasing the depth

of the catalyst bed had a different effect from increasing throughput to a bed of standard depth. A lower olefin content is observed with the deeper bed indicating the primary products to be olefinic, and normally undergoing more or less secondary hydrogenation, depending on the depth of bed.

As a part of the exchange of technical information between Ruhrchemie licensees it was apparently the practice to exchange copies of patent applications relating to the Fischer-Tropsch process. A number of these applications dating from 1936 to 1939 were captured (Doc 81) and brief abstracts thereof are attached as Appendix D. Probably the U. S. equivalents of some of these applications are among those seized and made public by the Alien Property Custodian.

Washing wax from the catalyst with a solvent at its boiling (or condensing) point, the subject of Brabag 182389, was apparently being practiced at Rheinpreussen. With this exception there is no evidence as to what extent, if at all, the procedures in question have been used. No applications of this character filed later than June 1939 were found.

H. Product Recovery

The condensible products from the first and second stages of synthesis were recovered in separate but essentially similar units comprising water scrubbing towers for cooling by direct contact with water and condensing the heavier oil, and batteries of charcoal absorption chambers for recovering the light benzine and C_3-C_4 hydrocarbons. Each charcoal unit consisted of seven towers, normally divided as follows:- 2 towers absorbing, 1 tower steaming, 2 towers drying and 2 towers cooling. The time cycle is as follows: absorption 40 minutes, steaming 20 minutes, drying 40 minutes, and cooling 40 minutes. The remains of some of the charcoal absorbers are shown in Fig. 24 and a more general view of the absorption plant is shown by Fig. 25. The charcoal was obtained from Lurgi at Frankfort. No significant data on the performance of the charcoal absorbers have yet been found.

Part of the dry gas (Rest gas) from the final charcoal absorption is returned to the gas cracking unit for conversion of its Methane and the balance is used as fuel. The distillate from the charcoal absorbers is stabilized to yield a light benzine bottom which is used as a blending stock for motor fuel, and a normally gaseous product overhead, consisting mainly of C_3 and C_4 hydrocarbons, which

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goes to the alcohol plant for utilization of its olefin content. This overhead is normally handled as a liquid under pressure and identified as "gasol". Except for the part used for alcohol manufacture it was apparently sold mostly as motor fuel under the less confusing name of "Treibgas". A diagram was obtained showing the arrangement of the original stabilizing unit (Doc. 31). A second stabilizing unit was built in 1939 when the capacity of the original unit proved inadequate.

The combined oil from the water scrubbers is fractionated to yield light and heavy benzin, light kogasin, middle oil, heavy kogasin, and a waxy bottoms known as "gatsch". Practically no information could be obtained about the properties or uses of these products except by subsequent study of seized documents. The opinion was expressed that the gasoline had an octane number of 66-70 but this was subsequently proved wrong.

An oil cracking unit had been erected in the Moers plant but was never used for the intended purpose. This was described as a Wilke unit, but subsequent study of documents indicates that it was a Carburol unit built by the Wilke Co. A complete set of drawings, including engineering calculations, for this unit was obtained (Doc. 26). The fractionating equipment on this unit had been used to supplement inadequate capacity of the primary fractionating plant, but the whole unit was dismantled and moved after suffering some bomb damage. Probably the desirability of using Kogasin as Diesel fuel instead of cracking stock was a factor in this move.

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