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CI REPORT 3260.

STRICTLY CONFIDENTIAL

Hydrocarbon synthesis
from
mixtures of carbon monoxide and hydrogen.

REPORT
on
Visit to and information received on Ruhrchemie Plant at Holten.

25th October till 1st December 1938.

VERY FULL TECHNICAL DETAILS.

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SUMMARY.

Due to the large amount of information obtained, this summary can only give an outline of some of the most important subjects. More detailed information on these and the other subjects is to be found in the report itself.

General description and capacity.

In Holten the synthesis gas is produced from coke in watergas generators. The watergas produced contains carbon-monoxide and hydrogen in ratio 1 : 1.25, whereas a ratio of 1 : about 2 is preferred for synthesis by Ruhrchemie, at least for synthesis at normal pressure.

After H_2S purification, therefore, 1/3 of the watergas is sent to a conversion plant, where the greater part of the CO is converted with steam into hydrogen and CO_2.

The mixture of converted and original watergas constitutes a synthesis gas with the desired CO : H_2 ratio and containing 15 - 17 % inerts. After being purified from organic sulphur down to max. 0.2 gr S/100 m3, this gas is sent to the synthesis plant.

This plant, in which the gas is treated in two stages with intermediate cooling of products between stages, consists of 52 converters operating at atmospheric pressure.

The capacity of the Holten-plant was given at 90 t primary product per day (34,000 t/year), for which about 35,000 - 40,000 m3 synthesis gas per hour are required.

72 High-pressure converters (5 - 10 atm. pressure) are being installed and will increase the total capacity of the plant to 85 - 90,000 t/year.

This part of the plant is gradually being put into operation.

For the production of the required watergas 11 generators with a total rated capacity of about 80 - 90,000 m3/h have been installed.

Yields and quality of primary product.

When working at atmospheric pressure, a yield of 120 grams liquid product plus 12 grams Gasol = C_3 and C_4 per m3 ideal synthesis gas (= gas consisting of CO and H_2 only) is obtained.

When working at higher pressures the yield increases to 145 grams liquid product plus 7 - 8 grams Gasol per m3 ideal gas. (Theoretically a yield of 205 g/m3 can be obtained if the CO is completely converted into liquid hydrocarbons).

Characteristics of products obtained when operating at:

	normal pressure	higher pressure (7 atm.)
I.B.P.	35° C	35° C
-100°C	28.5 % by wt	17 % by wt
-200°C	61.5 " "	42 " "
-320°C	88.5 " "	72 " "
O.N. Res. M of gasoline Endpoint 160°	57.5	39
O.N. Res. M of gasoline Endpoint 180°	51.5	32

Synthesis under pressure yields more total product, which at the same time, is heavier. The process under pressure requires more energy and no conclusion can as yet be drawn which of the two processes is to be preferred.

In Holten the primary product is worked up distillation and cracking.

Note:

For full details about the properties of the primary products obtained both at normal and at elevated pressure see Annex D (4 sheets).

These sheets have been taken from the Ruhrchemie's Report submitted to the U.S.A.C. partners according to Article IV of the agreement.

Catalysts.

The catalyst used consists of a mixture of Cobalt, thoriumoxide and magnesium oxide precipitated on Kieselguhr.

In Holten a large catalyst plant is available which serves besides Ruhrchemie's synthesis plant also several other Fischer plants in Germany. This plant regenerates spent catalyst together with a certain quantity of fresh materials to make up for losses, which amount to about 3 - 5% per year.

The metals are dissolved in nitric acid and, after purification of the solutions obtained, precipitated as carbonates on Kieselguhr as a carrier. The precipitate is dried and then reduced with hydrogen. The size of catalyst particles varies from 1 - 3 mm.

One synthesis converter holds about 10 m3 (= 3 tons) of catalyst containing about 850 - 900 kg Cobalt.

Catalyst life when operating at normal pressure amounts to 4 - 6 months

CHAPTER I.

FIRST MEETING I.G. LUDWIGSHAFEN

Tuesday 25th October 1938.

Present, from:

Standard New Jersey:	Scharmann Roetheli Spicer
Kellogg:	Keith Ward Johnson Ribblet Roberts Mansfeld
I.G.:	Pier Ringer Peters Hofeditz Wietzel
I.H.E.C.C.:	Tillmann Van 't Spijker
Shell:	Langen van der Valk Volkers.

Dr Ringer regretted to state that Ruhrchemie's report was unavailable for distribution, as consent of a certain authority had not yet been received, which, however, was expected any moment. Proposed to study report the next few days and after that visit Ruhrchemie at Holten.

The Ruhrchemie's report was handed over on Wednesday evening and it was agreed that on Friday Ruhrchemie would give further verbal information.

Friday and Saturday 28th and 29th October.

Present: same as mentioned above. Moreover from:

Ruhrchemie:	Feiszt
	Willke
I.G.:	Winkler
	Sabel
	Fritsche
	Meisenheimer.

The first subject to be discussed was the catalyst, the manufacturing of same and, subsequently, the purification of the gas and the catalyst plant proper.

CATALYST.

Information given by Dr Feiszt (Ruhrchemie).

HISTORICAL DATA.

Dr Feiszt started with a few historical data.

Ten years ago tests were commenced with Fe and also with Ni. Synth. gas ($CO + H_2$ in proportion 1 : 2), with Ni as catalyst, produced mainly saturated hydrocarbons with a rather large percentage of methane. Thereafter Co was used, with the addition of Cu, which allows working at lower temperature and reduction of catalyst in situ. This catalyst produces less saturated hydrocarbons and was the first to be used on a pilot-plant scale at Holten. Activity and lifetime of Co + Cu were rather small.

Therefore, Co-Th catalysts were tried out and with satisfactory results. In the meantime they had succeeded in reducing the catalyst in a special furnace and filling the reduced catalyst in the converters. This was a difficult problem, as the reduced catalyst is highly pyrophoric. Up to 18 % of Th oxide calculated on Co metal was used. The metals were deposited on Kieselguhr as a carrier and precipitated as carbonates or hydroxides. After drying, reduction with H_2 took place at temperatures between 350 and 400°C. Reaction temperature is lower than with Fe and Ni, with a smaller production of methane. The plant at Holten was started with this catalyst. Afterwards trials were started to replace ThO by MgO, the latter being cheaper and available in Germany. The results were satisfactory, if not better. The lifetime of Mg is 1 - 2 months longer and the formation of methane is also less than when using Th.

production In general it can be said that the composition of Ni, Fe and Co is different. Additions of Th and Mg to Co do not change the characteristics. The following figures may illustrate this:

		GAS CO : H_2 = 1 : 2		CO:H_2 = 2:1
		Co	Ni 2)	Fe 2)
	(I.B.P.	35°	35°	35°
refers	(up to 100°C	28.5 % by wt	34 % by wt	38 % by wt
to	(up to 200°C	61.5 "	72 "	80 "
liquid	(up to 320°C	88.5 "	95 "	98 "
products	(sp.gr.of fractions up to 200°	0.693	0.670	0.665
only	(% olef.of fractions up to 200°	35	15	42
	(acid content mg KOH/g prod.	up to 0.005	up to 0.005	roughly 0.1
	g $C_3 + C_4$ 1)	12	18	24
	g CH_4 1)	32	42	42
	g total product 1)	120	95-100	90-95
	CO_2	3	4	large
	useful reaction temp. range	185-198	190-210	210-240

1) per m3 normal synthesis gas
2) figures given from memory

The reaction temperature increases from the minimum to the maximum in the course of the run, which is for Cobalt-Th about 4 months.

The content of Th oxide can be varied from 10 - 20 % in relation to the metal Co. The same applies to MgO without important changes in the product. If the ThO and magnesium content is more than 20 % or less than 10 %, the activity decreases and also the lifetime of the catalyst. A higher Th content results in heavier products. No definite data are available regarding Mg. Low Th content entails higher temperatures, which, however, affect the lifetime unfavourably.

In general at higher temperature lower boiling products are formed; a Co catalyst at higher temperature increases $C_1C_3C_4$ production, whereas its lifetime is shortened.

THE CAPACITY OF THE CATALYST.

The average load on Co-Th contact for the yields reported is 1 m3 synthesis gas per kg Co/h. With Mg this can be 50 - 70 % more and such at a one to two months' longer lifetime. With fresh contact the load can be higher, e.g. 1.200, which decreases then to 0.800 at the end of the period.

x)

In fig. 1 curves I and II show the variation of yields against catalyst life for Co-Th catalysts at different, but constant loads of 1.0 and 1.5 m3 synthesis gas/kg Co/h respectively. Actually when running a plant the load is gradually decreased in order to obtain a more constant CO % conversion; this is illustrated in curve III for a Co-Mg catalyst.

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x) The figures of this chapter relate to annexes A, if not stated otherwise.

Throughputs of from 1700 - 1800 m3/h have already been attained. It has been proven advantageous to arrange 2 steps working on 70 - 75 % CO conversion in the first stage. A higher percentage of conversion in this stage would result in an abnormal production of methane and gasol. If a catalyst works very well and converts 90 % of the CO, it is possible to reduce the temperature which, however, will only help for a short time and it is preferable to increase the throughput.

SYNTHESIS AT ATMOSPHERIC PRESSURE.

In running a plant two different procedures can be followed: A converter can be placed in the first stage and after about 2000 hours in the second stage, or the converter can be kept for its whole lifetime in the first stage, using separate converters for the second stage only. The proportion of the number of furnaces in first and second stage will be kept at a constant figure in both cases.

For design purposes, when working at atmospheric pressure, the average load on the converters is taken at 750 m3/h in first and second step together. Per converter 850 - 900 kg of Co metal is used, which is equal to about 3 tons of catalyst with an apparent density of 0.26 - 0.30. At Holten all the "atmospheric" converters can be used for first and second stage. However, for future plants it would be sufficient to make arrangements that only 50 % of the furnaces can be connected either to the first or to the second step. Thus part of the converters are always used in the first stage, the CO conversion percentage being regulated by adjusting throughput and temperature. The important point for conditions in Germany is to arrive at a maximum overall yield of liquid products of the total plant. It is possible that other procedures will prove to be of advantage, especially as experience with the pure Co-Mg contacts is still insufficient.

INFLUENCE OF PROCEDURE ON QUALITY OF PRODUCTS AND CONVERSION.

1. The first factor of influence is temperature.

With Co-Th or Co-Mg contacts the starting temperature is about 180°. The products contain a rather large quantity of paraffin wax and a high percentage of products boiling between 140° and 280°C. As the catalyst gets older, the temperature has to be increased, resulting in a lower boiling range of the products. During the run the propane-butane production increases from 10 - 15 g/m3; at the end the temperature of the converter attains a maximum, producing still lighter products. The following figures will illustrate this:

first period	37 - 39 %	boiling below	150°C
middle period	47 %	" "	150°C
end period	55 - 57 %	" "	150°C

At the same time the olefine content and the acid figure show variations. The olefine content in the product boiling up to 200°C varies from 30 % in the beginning to 35 % in the middle and 40 % at the end. Variations in octane numbers are only slight.

These changes find their principal explanation in temperature variations. Ageing of catalyst is presumably of no influence.

2. Influence of variation of CO:H_2 ratio on products.

Increasing the CO:H_2 ratio from 1:2 to 1:1.8 results in a higher yield of olefines, e.g. of 5 % in the fraction boiling up to 150°C. The proportion between high- and low-boiling products changes only slightly; the octane number increases only by 1 - 3 points.

The % olefines in C_3C_4 increases from 50 to 60 - 65 % (a maximum of 72 % was found).

When decreasing the $CO:H_2$ ratio below 1:2, gradually more and more methane is produced, e.g. with a gas consisting of 95 % H_2 and 5 % CO, only methane is obtained.

3. Variation of the inert content.

More inerts increase the percentage of low-boiling products, for which reason in the second stage more low-boiling products are produced.

4. Effect of space velocity.

Higher space velocity results in production of lighter products. The question has been put whether the height of the catalyst layer can be increased. It was answered that 2½ m has been chosen on account of the experience in semi-technical experiments, also because this was the largest dimension that could be used in view of the size of railway waggons. The following graph gives an idea of the changes in product when applying a larger velocity.

The graph fig. 2 gives an idea of the change in production of one converter when increasing the space velocity. The curve shows a maximum, which, according to Dr Feiszt, for the atmospheric converters at Holten, will lie between 1,700 and 2,000 m3 throughput. ~~Refer also to annex B fig. 2~~.

Everything that has been stated above relates to working at atmospheric pressure. The temperatures mentioned are always steam temperatures in the boilers. It is estimated that the temperature of the gas flow is about 10 - 15°C higher. On the active catalyst centres the temperature will be still higher, maybe up to 100°C.

Reversing the flow of gas from downflow to upflow gave unfavourable results, which must be attributed to the fact that too much high-melting paraffin wax remains in the upper layers of the catalyst, finally resulting in clogging up of the converter.

The pressure drop in a converter on normal operation, which means downflow, is about 50 - 150 mm water. After 50 - 60 days' run a converter had already accumulated its own weight = 3 tons as paraffin wax. The dimensions of the converters are about 5 m long x 1.5 m wide x 2.5 m high. The free space in the oven is about 10 - 12 m3. The average load per oven is about 1000 m3 synthesis gas at 0° and 760 mm Hg.

RE-ACTIVATION OF CATALYST.

When working at a constant temperature (say 185°) the CO conversion falls off rapidly during operation. By gradually increasing the reaction temperature (say from 188 - 198°) this decline in activity can be partly counteracted, but still the CO conversion during operation of the catalyst decreases gradually. This is mainly due to the accumulation of paraffin waxes and resins. It is then necessary to re-activate the catalyst, which is done at Holten by replacing the synthesis gas flow by a flow of pure H_2 at temperatures of 200 - 210°C (see graph fig. 3). A re-activated catalyst gives a slightly lower yield than a fresh one and also the CO conversion shows a faster decline. The average activity is shown by the dotted line. In actual operation, in addition to the above, the throughput is gradually decreased in order to assist in keeping up the CO conversion.

The re-activation with H_2 results in a cracking of paraffin wax, yielding about 45 % of heavy oil boiling between 200 and 320°C and about 5 % gasoline, the balance being converted into methane. (When working at higher pressures (in the pilot plant), this re-activating has not yet been necessary, firstly because temperature increase is very slow; secondly because products formed partly condense and dissolve paraffin wax.

Re-activation can also be done by dissolving the paraffin wax and resins in heavy benzine, and also in benzol or acetone. In this way the total yield of the plant could be increased by about 1½ - 2 g/m3, because in this case no cracking occurs. However, this procedure is cumbersome and has only been applied in the low pressure pilot plant.

The Co-Th cat. produces about 1½ - 3 tons of wax per about 1000 hours per converter, the Co-Mg catalyst giving about 60 % of this quantity.

This re-activating procedure at Holten is repeated 3 to 4 times in about 4 months, after which the catalyst is removed from the converter for complete reworking in the catalyst plant.

SYNTHESIS UNDER PRESSURE.

Besides the synthesis at atmospheric pressure, a method has been developed for working under a higher pressure; the pressures applied at Holten vary between

5 and 10 atm. In general the influence of variations in operation under pressure have the same tendency to change the product as with atmospheric pressure. The products change in the same way as when working at atmospheric pressure. The operating temperature range is wider, being from 180 to 200° (probably even 210°). When working at 7 atm. with Co-Mg catalyst, a product with the following characteristics was obtained:

I.B.P.	35°
up to 100°	17 % by wt
" " 150°	29 % " "
" " 200°	42 % " "
" " 320°	72 % " "
spec.gr.of fraction boiling below 200°	0.690
olefine content " " " "	18 %
acid value	0.005 mg KOH/g
CO_2	> 2 g/m3
C_3C_4	7-8 g
CH_4	25-27 g
liquid product	145 g

It appears that there is no great difference in products between 7 and 10 atm.

The catalyst has a longer lifetime than at atmospheric pressure. It is estimated that the life will be increased by at least 30 %.

The temperature can even be increased to 210° without excessive production of methane.

The average throughput may be 15 - 20 % more than when working at atmospheric pressure. This figure is felt to be conservative.

Pressure experiments in pilot plants have been started from the beginning with Mg or mixed Th-Mg catalysts. The figures mentioned above relate to these catalysts. It may, however, be possible that for Mg alone the figure of 1200 can be surpassed. It is intended to start the full-scale high-pressure converters (expected in the next few weeks) with an initial throughput of 1700 m3/h.

Synthesis under pressure yields more total product, which at the same time is heavier. The process needs more energy for compression and no conclusion can as yet be drawn as to which of the two processes is the better. This will depend also on the prices of the various products obtained and the costs of electrical energy.

When producing gasoline as a final product, the products balances may be given as follows:

	prim.prod.		gasoline
a. L.P.	120 g	50 % straight-run up to 145°C	60 g
		50 % reformed at 73 %	43 "
	12 "	gasol polym. incl. pol. of gasol of cracked gases	5 "
			108 g
b. H.P.	145 g	20 % straight-run up to 125°C	29 g
		116 g reformed at 73 %	85 "
		+ polym. of gasol	6 "
			120 g

In both cases the final mixed gasoline has an octane number of 66. There is practically no difference between research and motor method.

The lifetime of the high pressure catalyst is not yet definitely known; 6 months may be accepted as a conservative figure. This lifetime relates to an average yield of 120 - 145 g. The catalysts are at present the same as with low pressure synthesis.

It was asked why the throughput could not be increased proportionally with increase of pressure. Dr Feisst stated firstly that the increase in throughput of 15 - 20 % given by him must be considered as very safe. The upper limit of increase in throughput has not yet been investigated. Secondly, although absorption velocity increases with pressure, desorption of the hydrocarbons produced from the catalyst surface seems to be relatively independent of pressure

<u>Energy consumption.</u>

For synthesis at atmospheric pressure at Holten, a blower is used, to deliver the gas at 3000 mm water-gauge. The capacity is 40,000 m3/h. The blower takes 600 kW. The figure in the report of 600 - 800 kWh per ton primary product includes all electrical consumption, assuming that all blowers, etc. are driven electrically. About 50 % of this is used for the gas production from coke at Holten.

In the Holten plant, for part of the energy, steam is used. The total steam production of the catalyst ovens would be sufficient for the production of all electrical energy and there would still be a surplus of about 400 kWh per ton of product. When working at higher pressure, the power consumption is much higher.

ORGANIC SULPHUR REMOVAL.

The purification of watergas is relatively simple, as practically no tar ~~and no ammonia~~ and no resin-formers are present in this gas. Inorganic sulphur is removed in the usual manner; organic sulphur is eliminated by passing the gas through a mass consisting of a mixture of iron oxide and sodium carbonate at temperatures of 200 - 300° in towers, where special care is taken to ensure a good gas distribution. Two types of these towers are in use:

In the first type the gas is passed through different layers of purifying mass in 2 towers which are connected in series, each tower containing about 65 tons mass. One set of two towers has a capacity of 20,000 m3/h.

When using a normal quality of German coke for the production of watergas, the organic sulphur content varies from 12 - 15 g per 100 m3. Every 83 days one tower is taken out of operation for renewing the mass.

For the organic sulphur removal, the so-called final purification, 5 sets of 2 towers are available at Holten. When one tower of a set is taken out of use, the other is also cut out. Each set of towers is equipped with a furnace for heating the gas and a circulation blower, to attain the necessary velocity in the pipe-heater, whilst the air for combustion is taken from a main line. The towers are also equipped with one heat-exchanger between the 2 towers, which, however, has been found to be not necessary.

Gases produced from bituminous substances like coal and lignite may contain resin and resin-forming substances. However, the latter will be destroyed at high temperatures of, say, 1100°; if the gas in the generators has been heated sufficiently, the resin-forming substances are cracked and eliminated. If elimination of resin-forming substances is impossible, an active charcoal unit has to precede the organic sulphur removal.

The purifying towers of the second type have cylindrical screens; two towers are connected also in series of two. The gas passes through the mass in the towers in a radial direction. This construction renders it possible to empty the towers through the centre and is to be preferred when no heavy hoisting equipment is available. At Holten a 30 ton portable crane is available, which is necessary for lifting the heavy inorganic sulphur-purifying boxes.

CONDENSATION.

The gas from the converters is passed through vertical coolers shaped as towers, where the water is injected in 3 stages. The towers are lined with acid-proof brickwork, which has to be finished very carefully, all supports being made of stainless steel. Water and condensed products are taken off in also carefully lined trenches. The water is kept in circulation and cooled in normal cooling towers constructed of wood, whilst care has been taken that all screws and bolts are made of stainless steel. The water-lines have to be made of alloy steel or of aluminium, as is done at Holten.

The temperature at the top of the tower is 27°, the condensed product mainly boils above 145°C. After the tower the gas is passed through a charcoal absorption plant of normal type. If it is necessary to attain a high yield of C_3 and C_4, a low saturation of the charcoal is necessary.

When desorbing (with steam), during the first 5 minutes the gas containing a large quantity of CO_2 is passed into the air. Then a gas containing about 60 % of C_3C_4 and 20 - 25 % CO_2 is driven out. This gas is compressed at 35 atm. and the condensate passed through a stabilizer. and the rest!

At high-pressure-synthesis, condensation is much simpler. The cooling procedure is then as follows: In the converters proper about 35 % of condensate is formed, with a boiling range of from 200 - 320°C. After separation, the gas is then passed through a simple pipe cooler with tubes of acid-proof alloy steel. It is possible to apply a hot soda-wash and thus avoid the use of special tube material; the price difference, however, is only small.

The very light fractions and also C_3 and C_4 are condensed in a normal oil absorption plant, dimensioned according to the necessity of producing more or less C_3 or C_4. At Holten active coal is used for this purpose, but only on account of the latter being available from the low pressure plant.

The acid content of the cooling water is about 200 - 400 mg per litre, consisting of organic acid and dissolved CO_2. The organic acid contains 70 % acetic acid, further formic- and propionic-acid.

It is possible to condense different fractions separately, which can be cracked separately. The tail gas from H.P. synthesis may be used (expanded) for generating electrical energy or for refrigeration purposes in stabilizers, etc.

After the first synthesis stage, the gas needs only partial cooling, thus condensing only the high boiling fractions, whereas the low boiling fractions pass on with the gas to the second stage. It is possible to pass the gas from the first stage through a charcoal absorption, freeing the gas entering the second stage from gasoline. Definite experience as to the desirability of the latter procedure is not yet available.

The absorption oil to be used, consists of a fraction produced in the plant itself.

The gas entering the second stage converters is not preheated.

MANUFACTURING OF CATALYST.

Every oven contains 10 (H.P.) and 12½ (L.P.) m3 of catalyst respectively, with an apparent density of 0.26 - 0.30. It is important that the catalyst should be dust-free. At present Holten's converters contain catalyst consisting of about 2 tons of Kieselguhr, one ton Co metal and 50 kg ThO and 80 g MgO. The quantities of ThO and MgO can be reduced, but definite figures are not yet available. The catalyst is manufactured in a separate plant, which has to serve two purposes:

1. manufacturing of fresh catalyst;
2. regeneration of used catalyst.

1. MANUFACTURING OF FRESH CATALYST.

A plant needs about 3 - 5 % fresh catalyst to make up for all the losses during the year, which figure is based on a re-generation frequency of 2½ times per year. The components of the catalyst are:

MATERIALS:

a. **Co metal.**

The Co arrives at the plant in the form of concentrate or as a metal (Belgian or German origin). The method of purifying and further treatment depends on the origin. The Co may not contain more than 0.2 % Ca and 0.5 % Cu. A certain percentage of Ni is necessary, say 0.2 %.

b. **Kieselguhr.**

Specific gravity 0.25 - 0.28 is normal. On a sieve of 400 holes/cm2 no more than 5 % may be retained.

The contents of Fe and Ca must be a minimum. German Kieselguhr, so-called "abgebrannt" or calcinated, is suitable as is also Kieselguhr of Japanese and American origin. If necessary, a chemical purification can be applied. It has been found that a certain but yet undefinable structure of the Kieselguhr is necessary.

c. **Thorium and Magnesium.**

These products are purchased in normal commercial quality; analyses may be had at Holten.

OPERATION.

Briefly the operation is as follows: The Co is dissolved in nitric acid, the solution is purified and, after addition of Th or/and Mg nitrate at a temperature of 90 - 100°, precipitated with sodium carbonate on Kieselguhr; the resulting mass is filtered and washed with hot distilled water, after which the wet catalyst is dried and granulated. The product is called "green corn" and has to be reduced with H_2 before use.

The flow during the manufacturing is roughly shown in fig. 4.

The water used for washing the filter cake must be very pure, and at Holten distilled water is taken for this purpose.

The nitrate solution is made by adding Co, portion after portion, to nitric acid in a stainless steel container, equipped with powerful stirring apparatus.

The green corn is produced in different sizes, e.g. 1 - 3 mm or 2 - 4 mm, etc.

Pulverizing has to be avoided as far as possible; dust is recirculated.

2. THE RE-GENERATION OF USED CATALYST.

As stated above, in the course of time the catalyst mass becomes less active, most probably on account of deposits of paraffin wax, resins and also tar. Moreover, a certain sulphur content is detrimental. The spent catalyst from the converters is transported in special vessels to the catalyst plant. If the catalyst arriving at this plant contains more than 25 - 30 % of paraffin wax, the latter has to be removed either by dissolving in benzine or by steam.

If the mass is still pyrophorous, it has to be oxidised first with steam or carefully with air; when using air high temperatures (say above 150°C) have to be avoided, in order not to decrease the solubility of the Th.

The catalyst mass is thereafter dissolved in batches in nitric acid. Vigorous stirring is necessary.

The slurry is passed to a filter press and the Kieselguhr removed.

For a simplified flow scheme see fig. 5.

The solution is then heated with a limited quantity of sodium carbonate, precipitating the impurities such as Fe, Cu, Al, part of the Mg and also Th. If necessary, the Th can be recovered afterwards; it may, however, be of advantage to return the Fe-Th compound to special industries.

In a second stage, by the addition of sodium fluoride, the surplus quantity of calcium is removed. This calcium originates most probably from the attack of nitric acid on the Kieselguhr. Apparently this Ca had no detrimental effect on the catalyst when fresh Kieselguhr was used.

Now a Co nitrate solution is produced, which has the same properties as when manufacturing fresh catalyst.

The Kieselguhr could also be recovered, but even at Holten it is considered better practice to replace it by fresh Kieselguhr, using the spent dry produc for other purposes, such as insulating, etc.

REDUCTION.

The reduction of the catalyst takes place at 390 - 450° and being an exothermic reaction it has to be accomplished in the shortest possible time, as the contact is unfavourably affected by high temperature.

The flow through the reduction plant in a simplified form is given in fig. 6.

An excess of H_2 is circulated, containing no CO, CO_2 or water. The circulating hydrogen is dried in a very extensive and careful way.

From the C of the carbonates a certain amount of methane is formed, which has to be bled off continuously.

The CO content of the fresh hydrogen gas is limited to 0.05 %. A larger amount would entail the formation of methane, whereby the heat produced would burn (sinter) the catalyst.

The green corn may not be too dry (water content about 10 %); with drier green corn practice has shown that the catalyst produced is less active.

Using air for the decomposition of carbonates would necessitate too high a temperature.

The methane content in the circulating gas should not exceed 1½ - 3 %; it is not the methane itself that is dangerous, but the formation of methane. Even if no methane should be formed, a certain quantity ~~of hydrogen in circulation has to be blown off as other~~ yet unknown detrimental substances are being formed. About 1000 m3 circulating gas per square metre per hour of catalyst surface is used.

The reduction takes place in vessels with a screened bottom, having a surface of 1½ m2, on which the green corn is spread in a layer 35 cm thick.

The flow is as in fig. 7.

After the reduction is finished, which takes about one hour, the catalyst is cooled with circulating nitrogen. By turning over the vessel the catalyst is discharged (without coming into contact with air) into a container, which can take about 16 charges, and saturated with carbon dioxide.

MANUFACTURING OF THE MASS FOR THE FINAL PURIFICATION.

For final purification a mass is used, consisting of lux mass and sodium carbonate. Lux mass, being mainly iron oxide, is left over from the manufacturing of aluminium from bauxite.

In a special mixer this lux mass, containing 50 - 60 % water, is mixed with dry sodium carbonate in the proportion: 2 dry lux mass to 1 soda. The plastic product obtained is transported to a so-called "Strangpresse", which produces short macaroni-like pieces, from which, in a revolving hot air drier, the water is removed. The resulting product should contain about 12 % water and is placed on a sieve mechanism, from which the dust is returned to the original mixer. The size of the end product is about 5 - 15 mm; it can take up about 10 % of its own weight of sulphur. After use this mass is not re-generated.

Fig. 8 shows a simplified flow of the manufacturing process.

CHAPTER II.

VISIT TO THE RUHRCHEMIE PLANT AT HOLTEN,
on Monday, 31st Oct. 1938.

Present: the parties from Standard, Kellogg, I.G. and Shell, as mentioned before.

Furthermore from Ruhrchemie:

Director Alberts
Drs Feiszt
Wilke
Bahr
Von Asboth
Schaller

The works at Holten (Ruhrchemie and Ruhrbenzin) consist of the synthesis plant proper, a large ammonia plant, a separate plant for manufacturing catalysts, which also serves some 4 other synthesis plants in Germany, laboratories, pilot plants and auxiliaries.

The synthesis plant combined with blue water-gas plant has an extensive lay-out, separated from the other plants. The production of the synthesis plant at the time of the visit was given at 90 tons primary product per day, or 34,000 tons per year, with a gas throughput of about 32,000 m3/hour. It was expected that within a few weeks the first units of the pressure synthesis plant would be put into operation. After completion of this pressure plant the production will be increased to 85,000 - 90,000 tons of primary products per year.

The manufacturing of blue watergas.

Eleven Demag generators, system Humphries, Glasgow, were installed, 6 of which have a rated capacity of 6800 m3/hour each, the 5 newer units having 7800 m3/hour. In actual operation these units produce 7400 and 8500 m3/hour each respectively. Four units were in operation with one as stand-by. The generators are operated automatically, which gave full satisfaction. Coke is charged to the generators every 3 minutes at the rate of 200 kg, i.e. about 100 tons per 24 hours. The cycle is:

1	minute	blowing with air
1	"	blowing steam from top
1	"	blowing steam from bottom.

The composition of the gas produced was given as follows:

6 % CO_2
40 % CO^2
50 % H_2
0.6% CH_4
3.4% N_2

The pressure in the generator was about 900 m water, with a water seal at the bottom of the furnace.

Each furnace is equipped with one 18 atm. steam boiler for waste heat, while at the same time the furnace jacket produces low pressure steam (2½ atm.), used for blowing the furnaces.

Extensive equipment was available for the transportation of the coke in special railway containers (4 containers of 10 tons each upon 1 railway carriage) to bunkers on top of the generators.

A

After the generator plant comes the CO conversion plant, where about 1/3rd of the total gas output, after sulphur purification, is passed over a catalyst together with steam, to convert the CO with steam into CO_2 and hydrogen, thus producing a gas with a higher H_2 content, which, after mixing with the untreated 2/3rds, yields the synthesis gas of about the following composition:

13.5%	CO_2
28 %	CO
55 %	H_2
0.4%	CH_4
3.1%	N_2

The conversion is effected catalytically at a temperature of about 450°C. This plant was originally placed before the final purification; afterwards this was reversed on account of difficulties encountered with the converter catalyst (see figs 9 and 10, Annex A). 2

Next to the CO conversion plant a turbo compressor station was in course of erection. In a building of about 15 x 65 m, equipped with a 15 ton crane, four turbo compressor units, each unit consisting of one l.p. and one h.p. compressor, are placed. The l.p. compressors have a working pressure of 5 atm. and a capacity of 20,000 m3/hour at 3,000 revs/min. The electric motor of 2000 kW at 1500 revs/min. is connected to the turbo by a gear-box, manufacturer Deutsche Werke; the turbos are from Gutehoffnungshütte; the motors from Siemens.

The high-pressure compressors have the same capacity and are of the same type and make, the delivery pressure being 10 - 14 atm. The motor is rated 1000 kW. One unit of two compressors is driven by steam, produced by the above-mentioned 18 atm. boilers. The lining up such that two units are used for water gas and one for converted gas, whereas the fourth unit is stand-by for both purposes.

H_2S and organic sulphur removal plant.

Inorganic and organic or final purifiers are set up in one line, the whole space being covered by a 30 ton travelling crane, with an extension on one side over a free space and a railway track for emptying and refilling the screen-boxes. At one end of the purifiers a blower station is built (at the other end a filling station for bottled gas).

In this blower station 3 blowers of 40,000, 40,000 and 80,000 m3/hour capacity respectively are installed. Only one of the first-mentioned blowers was running, passing the gas from the gasometer (capacity 20,000 m3) through purification, converter and subsequently synthesis (see fig. 10, Annex A).

The delivery pressure is about 3.4 m water. Each blower has 2 stages at 3000 revs/min., coupled by a gear-box (in the same way as the compressors mentioned before) to an electrical motor of 640 kW (one blower of 40,000 m3/hr) or to steam turbines (one blower of 40,000 and one of 80,000 m3/hr).

Difficulties were encountered on account of sulphur depositing on the vanes of the blowers, which necessitated a shut-down every 8 weeks.

For this reason a change of the flow was intended, i.e., passing the gas through the H_2S purifiers before it enters the blowers. In Annex A. fig. 9 shows the gas flow when starting the plant, fig. 10 as it is now and fig. 11 as it is intended to be in the future.

In the blower station (dimensions about 24 x 20 m) also a steam-reducing station was installed.

The gas leaving the blowers at a temperature of about 60°C passes through a set of coolers with direct water sprays and then enters the H_2S removal towers. These towers are of the common type, as used in coke gas oven plants.

Two sets of 4 towers are available at Holten, the gas passing 3 towers in series, one tower of the set being refilled. Each tower has 16 screens with purifying mass in layers of 400 - 500 mm.

The Lux mass in these towers should not contain more than 50 % water; when preparing this mass, about 20 % spent mass is mixed with fresh mass, so as to obtain a better porosity. The average H_2S content of the inlet gas is about 3 g per m3; the purified gas contains 0.2 g H_2S per 100 m3 and, in addition, 150 - 200 mg organic sulphur per m3.

The organic sulphur removal plant, consisting of 5 sets of 2 towers each, of which one set is spare, is equipped with one heater per set, using tail gas and air, both from a main line.

A circulation blower serves the purpose of increasing the fuel gas velocity through the gas heaters.

These gas heaters are equipped with vertical tubes and as the gas enters from one side, thus heating the tubes direct exposed to the incoming gas, more than the others, it was necessary to provide for a separate expansion for the first half of the tube bank. Thus the outlet-cover on the top consists of two halves, each having a separate flexible outlet connection with separate balancing weights.

Two types of towers are in use, described fully in the Ruhrchemie report. The price of the flat screen towers is somewhat higher than the price of the cylindrical screen towers; moreover, the first type needs a hoisting equipment, but the flat screen towers can be recharged in 4 - 6 hours, whereas this takes 36 hours for the cylindrical towers.

Oxygen is introduced before the H_2S removal boxes, in such a quantity that the gas contains 0.3 - 0.5 % total oxygen as a maximum.

As inlet and outlet for each layer can be closed independently, it is possible to operate with two or more layers in series.

The synthesis plant.

The synthesis plant is housed in a large building about 170 m long and 35 m wide. A platform at a height of about 5 m crosses the building in the centre from one end to the other, the converters being situated left and right of this long corridor.

In the older half length of the building the l.p. synthesis ovens are placed.

In the centre an ample space has been reserved for operating control (central operating room).

In the newer half length of the building the h.p. synthesis ovens were partly ready and partly in course of construction.

As the overall length of the converters is only about 6 m, an ample space is left alongside the walls (open from the base to about 2½ m height) for a railway track on which the catalyst-containers are transported.

The weight of the large containers (dia.

3100 mm) is 5600 kg, taking one oven filling of catalyst (10 m3 is 3250 kg, or, if heavily loaded with paraffin wax, 5000 kg). The capacity of the crane travelling over the ovens and railway track is 15 - 65 to ! 17 tons.

A special ring equipment is available for tipping the container above the oven.

When an oven has to be emptied, a special scraper conveyor is attached to the bottom, from which with a bucket conveyor at the back of the oven, the mass is transported to the container. Vide Annex A, fig. 12.

At Holten 52 l.p. ovens are available, of which 48 - 50 are in operation, whilst 2 to 6 are out of use on account of changing catalysts and at the same time overhaul of auxiliaries, etc., also for re-activating the catalyst with pure hydrogen.

At Holten sets of 2, 4 and 6 converters are connected to one steam drum. The temperature of each oven is regulated from the central operating room by adjusting the pressure at which the boilers deliver their steam to the central steam line.

The boilers are designed for a working pressure of 30 atm. The normal pressure in the central steam line is 9 - 10 atm. When an oven with fresh catalyst is started, the temperature corresponds to about 5 - 7 atm.; during this short period of a few hours the steam is blown off in the low pressure line.

Feed of boilers is automatically controlled by Hanomag feed-water regulators, which work quite satisfactorily. The feed-water is softened in a permutite plant and the water is afterwards heated to 70°C, where under a vacuum all carbon dioxide and air are removed.

Quantities of inlet and outlet gas to and from each separate converter are measured.

Of the 48 - 50 ovens in use, 36 are connected in first stage and 12 - 14 in the second stage. These figures, however, may be altered to 32 in the first stage and 16 in the second stage, depending on the "newness" of the catalyst.

The gas enters the synthesis converters with a temperature of about 200°C, which, however, varies with the required temperature of the organic sulphur removal, the latter depending on the catalyst age.

The outlet gas of the first stage, with a temperature of 180 - 200°C, enters the intermittent coolers with direct water spray, of the same construction as the second-stage coolers mentioned further on, where about 50 % of the total liquid products formed in the first stage are condensed.

At Holten, where the capacity and the line-up of the charcoal plant do not allow of treating the total quantity of gas after the second stage, the cooled gas of the first stage is then passed through a set of 4 charcoal adsorption vessels and from there, via a water-cooler, to the second stage . This water-cooler had to be installed afterwards to equalize the outlet temperature of the charcoal plant, which changes during the adsorption period; the temperature of the gas entering the second stage is about 25°C.

122 [illegible]

After leaving the second stage, the gas is cooled again in a water spray tower and passed on to another set of charcoal vessels to be stripped, up to about 80 % of the C_3C_4, thus 20 % being lost in the tail gas. Further details about the condensation and the charcoal plant will be given below.

It was stated that the complicated construction of the l.p. ovens, which does not allow of much tube expansion, was nevertheless very satisfactory. In the course of 2 years' running, only very minor repairs to the oven-tube systems had been necessary. For these tubes normal seamless boiler tubes with tensile strength of 45 kg/mm2 are used.

To avoid leakages it was said that the oven was brougth up to temperature slowly (24 hours) and taken out of use also gradually. On a later occasion this was contradicted, when it was stated that the whole process of taking the oven out of use, dropping the catalyst, filling it up again and bringing the oven into production, required no longer than 48 hours.

? 12 hours

As already stated, an oven with fresh catalyst is started at a temperature corresponding to a steam pressure of 5 - 7 atm., which in the course of about 4 months is raised to 15 atm.

The steam pressure controls were said to be exact within limits of 1/10 atm.

When filling a new oven with catalyst, special care has to be taken to leave only a minimum of free space.

A surplus filling of, say, 1/2" on top of the tubes and cooling fins would entail excessive formation of methane and excessive heating of the top layer, with the resultant danger of burning of the catalyst and clogging up of the oven.

The catalyst building has room for 72 h.p. ovens.

The operation of the [illegible]

3448. Doc [illegible] [illegible] 1:10

See fig 3 Doc. 4

[illegible] [illegible] [illegible]

45 . 200-210°

[illegible]

000306

[illegible] 60% [illegible]
[illegible] Co-Th

MP [illegible] for [illegible]
[illegible]
[illegible]

[illegible]

NP Condensers Fluid [illegible] [illegible] - stainless steel /
fittings

MP " 35 (200-320°) [illegible] in
oven. [illegible] cooler of alloy steel.

Cat (1938) 100 : 5 : 8 : 200

~~[illegible] Co [illegible] 0.2% Cu 0.5% [illegible]~~

0.2% [illegible] necessary

Manuf Co + Th + Mg [illegible] [illegible]
[illegible]
Kalg. similtaneous

[illegible] # 1500

K [illegible] would [illegible]

[illegible] is less [illegible]

Time 1 hour [illegible] 450 1500 m³/m²/day

The operation of the converters is controlled by registering the CO_2 percentage of inlet and outlet gas. As average figures the following CO_2 percentages were given:

inlet first stage	13 %
outlet " "	32 - 34 %
" second "	45 - 47 %

On entering the first stage the gas has a pressure of about 1500 mm and on leaving: 1100 mm; on entering the second stage: 1000 mm and on leaving this stage: 650 mm.

Condensation.

The condensation after first and second stages of the low-pressure synthesis is effected in vertical cylindrical towers, of which 2 with a diameter of about 4 m and 1 with a diameter of 5 m is available, filled with Raschig rings 90 x 90 mm, with direct water sprays.

The condensate, together with the cooling water, is piped to settlers, where the product is separated and from where the water is re-circulated via cooling towers. The acid content of the circulating water is kept at an equivalent of 650 mg KOH per litre, by discarding 15 - 20 m3 water per hour per stage; make-up water is added at the upper inlet of the coolers.

All parts coming into contact with these liquids are made of acid-resisting material, as the products contain CO_2 and small amounts of fatty acids.

In the newly built part of the cooling plant product and water are separated in acid-proof brick-lined trenches.

At the Holten plant all valves in the gas lines (partly riveted, partly welded) are hand-operated, even to diameters of 1500 mm.

The charcoal adsorption plant, consisting of 5 adsorbers for first stage and 6 for second stage, (for the low-pressure synthesis plant). For the H.P. 4 new adsorbers were installed, built by Bamag (Lurgi system) and fully automatic (the valves operated by hydraulic pressure and controlled by electrically-driven camshaft). This system was said to be the first of its kind and gives complete satisfaction.

The adsorption vessels are placed on a structure of about 5 m height. The small vessels contain about 20 m3 = 8.7 tons of activated charcoal; the large ones have a capacity of 40 m3 = about 18 tons Valves and connecting lines are arranged under the vessels.

The charcoal plant is running with the following cycle:

	1st stage	2nd stage
adsorbing	40 min.	20-60 min.
steaming	20 "	20-20 "
drying	20 "	40-20 "
cooling	20 "	40-20 "
	100 min.	120 min.

When steaming, the first part of the gas expelled, with a high CO_2 content, is blown off. Then the vapours are cooled while the uncondensed C_3-C_4 go to a gasometer and are afterwards compressed at 35 atm. and cooled, the condensate being stabilized. 2.

The charcoal takes up about 4.5 % of its own weight when removing gasoline and (80 %) C_3-C_4.

Up to now 500 kg product per kg charcoal have been produced, whereas a figure of 800 kg has been guaranteed. The opinion was expressed that charcoal is very sensitive to resin-forming substances and paraffin mist, because these products cannot be removed by steam. in the charcoal-vessels!

In the charcoal plant at Holten the coal rests on aluminium screens. No difficulties were encountered with clogging up of same; on opening the vessels only very slight pulverization of the charcoal was found.

The effect of the charcoal after the first stage on the CO_2 content of the gas entering the second stage is rather small. When the gas entering the charcoal has 30 % of CO_2, it enters the second stage with not less than 27 %. This proves that the greater part of the carbon dioxide is not retained by the charcoal.

Drying and cooling of the charcoal is done with tail gas, the temperature during drying being 130 - 140° and during cooling as low as possible. When cooling the tail gas in circulation with water, the amount of cooling gas is equal to the amount of treated gas.

CHAPTER III.

MANUFACTURE OF RUHRCHEMIE CATALYST

Visit to and discussions on their catalyst plant on 31/10/1938, 14/11/1938, 17/11/1938, 18/11/1938, 21/11/1938, 30/11/1938.

A. Manufacture of fresh catalyst.

B. Regeneration of spent catalyst.

A. The various steps are:

1. Dissolving Co and Th and/or Mg in nitric acid.
2. Mixing the above solution with an equal volume of sodium carbonate solution containing 103 g Na_2CO_3 (water-free) per litre.
3. Addition of Kieselguhr.
4. Filtration and washing of the precipitated catalyst.
5. Addition of dust.
6. Further filtration and extruding of catalyst.
7. Drying of catalyst.
8. Screening and granulation.
9. Reduction.

See Annex A, fig. 4, for the flow of materials from points 2 - 9.

B. The various steps are:

1. Dissolving of spent catalyst in nitric acid.
2. Filtration of solution to remove Kieselguhr.
3. Addition of so much Na_2CO_3 until all thorium, aluminium and iron ~~and [illegible]~~ are precipitated (these latter impurities result from the fact that part of the Kieselguhr dissolves in the nitric acid).
4. Filtration of solution.

5. Addition of NaF to remove calcium as CaF_2 and/or magnesium as MgF_2
6. After filtration the solution contains about 45 g Co per litre. Magnesium and/or thorium nitrate are added and so much water that the final solution contains 40 g Co per litre. This solution is further treated in the same way as described under A.

See Annex A, fig. 5 for the flow of materials from points 1 - 6.

Discussions of the various steps.

As fresh catalyst is only made once when starting up a new plant and from that time onward the catalyst plant will treat spent catalyst only, we are starting our description with the much more complicated production of catalyst mass from spent catalyst. Make up for Co losses is added to the spent catalyst.

1. Dissolving spent catalyst.

This is done in sichromal containers, having a volume of 32 m3, with technical nitric acid of technical strength (about 620 g per l). These containers are equipped with cooling coils and, although they do not contain indirect heating coils, facilities for adding direct steam are installed. In newer catalyst plants indirect instead of direct steam is used for heating. The dissolving procedure is as follows:

About ~~(12 - 15)~~ 6 - 8 m3 $Co(NO_3)_2$ solution having a concentration of 55 - 65 g Co/litre is introduced into the tank. Then alternatively batches of about 100 kg of spent catalyst and nitric acid are added. The addition of nitric acid is measured by rotameters and so much is added each time that the free acid content never rises above 5 %. This is done to prevent

(~~the formation of a metal oxide difficult to dissolve and, further, to prevent~~) too great formation of NO and NO_2. During the dissolving process spent catalyst and acid are mixed by a stirrer having a V_2A-lined shaft and V_2A-propellers. The stirrer is driven by a ~~20~~ kW motor. As mentioned above, the solution is heated with direct steam. In the beginning the temperature is kept at about 55 - 60°C. From time to time a sample is taken and filtered, the Kieselguhr being analyzed on its Co content.

As dissolving proceeds, the temperature is gradually raised until the undissolved Co on Kieselguhr is less than 0.1 % of the total Co. Normally the final temperature should not exceed 9~~8~~0°C.
90°

Duration: 20 to 24 hours.

In Ruhrchemie's catalyst plant there are 10 such containers, each having a capacity of 2 ~~1~~ ovenfillings or about 6 ~~3~~ tons of catalyst giving about 25 - 30 m3 nitrate solution on dissolving. During this dissolving procedure about 4.5 % HNO_3 of the acid added (calculated as N_2) is lost to NO and NO_2. In the beginning these vapours were let off into the atmosphere outside the catalyst building. After some experimenting, e.g. trying to remove these vapours by injecting steam into the vapour lines, they are now installing the following equipment. Each of the dissolving containers is connected with a header, through which all vapours formed during the dissolving step are carried away by a V_2A blower after passing a spray vessel, which is meant to remove most of the NO and NO_2 vapours by water, the vapours entering this vessel at the bottom, water being introduced at the top through nozzles and continuously withdrawn.

After all Co has been dissolved, the solution contains 70 - 80 g Co/l and this solution + Kieselguhr is run off into wooden tanks, in which the slurry is stirred continuously (20 r.p.m.). These tanks are not necessary from a chemical point of view, but are merely hold-up tanks to allow smoother operation.

2. Filtration of Kieselguhr.

From these tanks the solution is pumped to filter presses with pitch pine frames. There are 16 of these filter presses at Holten, 12 of which are in operation. As filter material cotton is used, which apparently lasts very long. Since starting operations only 80 frames have been fitted with new cloth.

The filter cake of Kieselguhr is washed with tap water. About 30 m3 water is used per ton Co. The first part of the wash water leaving the filter presses is added to the filtered solution of $Co(NO_3)_2$. When a concentration of 21 Bé is reached the rest of the wash water ~~is~~ was run off into precipitation tanks in which various wash waters are collected. By adding Na_2CO_3 the dissolved Co is recovered as carbonate. After filtration this carbonate is added to the spent catalyst in the dissolving tanks. About 6 % of the total Co recirculates in that way all the time.

The mixture of the first part of the wash water and the filtered solution has a concentration of 55 - 65 g Co/l. From this solution a small quantity is introduced into the dissolving tanks before starting dissolving spent catalyst in nitric acid as mentioned under 1.

2. Precipitation of Mo, and Impurities (Fe, Al, [illegible].

The above solution is run off into wooden tanks with stirrer. MgO, which is lost later on in the process of regeneration, generally is added at this point. From these tanks the solution is pumped via storage tanks made of sichromal and via a heater, where its temperature is raised to 60 - 70°C, into a small (2 m3) wooden tank together with a Na_2CO_3 solution containing 103 - 104 g water-free Na_2CO_3/l and having a temperature of about 50°C. This temperature is obtained merely by means of the dissolving heat of the Na_2CO_3.

The Co solution still contains some nitric acid from the dissolving step. So much Na_2CO_3 is added in the small wooden tank that a pH = 4 is obtained.

The operation is carried out in such a way that measured streams of the two solutions come together just ~~before~~ entering the small tank, the contents of which are stirred vigorously. Excess Na_2CO_3 at any point of the solution must be avoided in order not to precipitate any Co, which will then be lost together with the impurities. From this tank the solution runs into large wooden tanks where some more Na_2CO_3 solution is added until a pH of 5.8 - 6.0 is obtained. The pH is checked by means of paper slips impregnated with indicators and each showing 6 various colours for compairing the indicator colours at 6 different pH values, for instance at pH values of 3.9 - 4.2 - 4.5 - 4.8 - 5.1 - 5.4 or at pH values of 5.2 - 5.5 - 5.8 - 6.1 - 6.4 - 6.7. These papers are, for instance, manufactured by Dr.Kloz (Leipzig) and called "Lyphan". Then the solution is left in the tank for about one more hour, while being stirred, and is thereafter immediately filtered; For this purpose a large filter capacity exists ~~was installed~~ at Holten. This procedure is discontinuous.

Most important during this purification step is to obtain a precipitate which can be readily filtered. Conditions as regards temperature, concentration, degree of stirring should be very carefully supervised in order to obtain good filterable crystals.

Annex A, fig. 14 shows a sketch of this arrangement.

The amount of Na_2CO_3 added in this step is about 15 - 20 % of the total quantity of Na_2CO_3 used in the manufacture of the catalyst. Besides the impurities all thorium, Pb, Bi and most of the organic substances ~~is~~ (are) precipitated in this step.

The wash water used for washing this filter cake is taken from the second part of the wash water used in a further stage for washing the final catalyst after being precipitated on Kieselguhr. The amount of filter cake being small, all wash water used for washing this cake is added to the filtered solution, which reduces its concentration from about 55 to about 48 g Co/l.

4. The filtered solution is run off into a wooden tank and stirred slowly by a stirrer with 18 r.p.m. NaF (~~dissolved in~~ water) is then pumped into this solution. As NaF does not dissolve well in water, it forms a suspension (which is pumped through iron pipes). So much NaF is added that all calcium and about ~~50 %~~ 40-50% of the magnesium is precipitated. This precipitation of Mg is necessary in order to obtain a ~~precipitate which can be filtered well.~~ As this magnesium is lost, it, therefore, has to be added somewhere before the removal of the calcium, i.e.

either before the precipitation step of Fe, Al, etc., as already mentioned, or before this step. It is evident that the amount of magnesium which has to be supplied for this precipitation will depend on the amount of calcium present. The ratio MgO : CaO should be at least 3 : 1. If the catalyst contained already Mg, which all newer catalysts do, then the Mg lost in this precipitation step can also be added afterwards.

The final solution should not contain more than 0.2 ~~% by weight Ca calculated as CaO.~~

The precipitation was formerly done at a temperature of about 55 - 60°C. Now the temperature is kept about 30°C and should not rise above 40°C. It was stated that this decrease in temperature was effected only to obtain better crystals.

Per ton Co about 100 -120 kg NaF are added at Holten.

The addition of NaF is controlled by analysis.

Just before filtering the CaF_2 and MgF_2 a small amount of filter aid, such as, for instance, Hyflocel, is added.

Duration of precipitation: 12 hours.

As formerly no good precipitate was obtained when adding NaF to the solution with pH = 5.8, HNO_3 was added first to the solution before introducing NaF, in order to lower the pH to 3.8.

Towards the end of this precipitation step Na_2CO_3 solution was then added to the mixture in order to raise the pH again to 5.8. Introducing HNO_3 has only been omitted for a few weeks past.

Filtration is done by means of a filter press which is made of ~~iron~~. The filtering material is cotton, covered with paper, the reason for this paper being only to save the cotton, as now paper plus filter cake are thrown away, whereas otherwise scraping the filter cake from the cotton would smear the jelly filter cake into the cotton openings. /wood.

The filter cake is washed with the second part of the wash water used for washing the final catalyst after its precipitation (see further on). Amount of wash water used: 3 m3 per ton Co.

Lately experiments have been started in order to see whether the removal of CaF_2 can be accomplished by decanting. No results are known as yet.

5. Not absolutely necessary, but more as a check on its final purity the solution, after being purified from Ca and having a pH = 5.8, is run off into wooden tanks of 30 m3, where a very small additional amount of Na_2CO_3 is added to precipitate any impurities which still may be present in the solution. The pH is thereby raised to 6.1. The solution is then once more filtered through a filter press and run off into/so-called adjusting/tanks, discussed further on under point 10. [illegible]

6. Dissolving of fresh Co.

Attached is Ruhrchemie's prescription with specifications for Co. ~~(Annex B Nº 3)~~. In no case should zinc and lead be present therein as they apparently cannot be removed; at least Ruhrchemie do not know any method of doing this.

When buying the oxide one has to be extremely careful, as oxides which have been heated at high temperatures do not dissolve or dissolve only partly and slowly in nitric acid. In such a case diluted nitric acid works better than the concentrated acid. At Prof. Fischer's laboratory in Mülheim it was found that when dissolving spent catalyst in strong nitric acid, a black substance was formed, which, on analysis, proved to be CoO. This oxide could only be dissolved very slowly , and was found to dissolve better in diluted acid.

Dissolving fresh Co for making the first batch of catalyst is done with about the theoretical amount of nitric acid, e.g. 1.05 - 1.1 parts per part Co.

The procedure is as follows: All HNO_3 needed for one batch is introduced into a dissolving tank and then the total amount of Co is added either as powder, in which case 35 % HNO_3 is used, or in melted form, which allows the use of 50 % HNO_3. The dissolving tank is equipped with cooling coils, whereas heating can be done with direct steam. The temperature is kept at a maximum of about 90°C. At the end of the dissolving process some more Co and then Na_2CO_3 are added to raise the pH to 6.1, which will precipitate any dissolved impurities. Maximum 10 - 15 kg Na_2CO_3 should be used per 4 tons Co. The contents of the tank are then sucked up by means of a vacuum and pumped via a filter press into storage tanks. Some undissolved Co will also be carried along by the solution, which will be removed, together with the impurities, by the filter press.

The filter cake is washed with distilled water and the wash water added to the mother liquor in the storage tanks.

After about 10 - 15 of such dissolving tank batches have been filtered, the entire filter cake is returned to the dissolving tank and the Co dissolved in diluted (35 %) HNO_3. The material which finally remains undissolved in the tank at Holten is returned to the manufacturer from whom Ruhrchemie buy their Cobalt.

The excess of Co in the dissolving tank and the Co on the filter press will remove any Cu which might be present in the Co metal and which otherwise would remain in the $Co(NO_3)_2$ solution after being dissolved in the HNO_3 together with the Co.

In the step of dissolving spent catalyst some Co is added from time to time as make-up for unavoidable losses in preparing and handling the catalyst.

I. Dissolving of magnesium.

There are no special prescriptions for the magnesium. Various market products have been investigated at Holten, i.e. cheap, expensive, pure and impure ones. After having started with pure ones, it was found that impure magnesium products could also be used. However, in general it can be said that the purer the magnesium, the better the catalyst.

Most important is that no impurities are present in the magnesium which cannot be removed in the purification step. Calcium should not be present when preparing the first batch of catalyst, as this is about the worst impurity conceivable. The SO_4 ion might be present in small quantities.

Dissolving of magnesium compounds in nitric acid is done in a separate step in ~~wooden~~ tanks without any difficulties. The usual concentration at Holten is about 120 g MgO/l. However, this concentration does not matter very much.

8. Dissolving of thorium.

Thorium has been obtained thus far from the Auer Company in sufficient purity. The amount of SO_4 ion should be limited and can be controlled by the washing when manufacturing this metal, as it is made via the sulphates. In the beginning the thorium contained too much SO_4 but since discussing this problem with the Auer Company a sufficiently pure metal has been obtained. The reason for limiting the SO_4 content is because thorium sulphate will precipitate when heating the nitrate solution, which apparently causes trouble by deposits in pipelines and valves. Furthermore insoluble K-or-Na-Th double salts can also be formed.

Zinc and lead should not be present, for the same reason as mentioned above when discussing cobalt.

The thorium compound bought from the Auer Company is a basic carbonate. However, as nitrate it can be used just as well. The first thorium bought by Holten did not contain enough water, which apparently is important in dissolving the thorium. Holten now buy a product with so much thorium that the basic carbonate contains ~~about~~ 70 % thorium calculated as ThO_2.

Also in this case it can be said that the purer the thorium compound, the more active the final catalyst.

Another compound which should not be present from an economical point of view is iron. It does no harm in the catalyst when freshly made, but one pays the thorium price for the total amount of metal present in the thorium compound; moreover, the removal of the iron in the first precipitation step costs sodium carbonate.

The concentration of ThO_2 in the nitrate solutions made at Holten is about 150 g/l.

The price of pure thorium in Germany is about RM 18.- per kg thorium calculated as ThO_2, i.e. RM 18.- for so much thorium as would give 1 kg ThO_2.

9. Kieselguhr.

Some general prescriptions will be given for the Kieselguhr. It should be

a. as pure as possible;

b. available in large quantities of uniform structure;

c. as light as possible;

d. as cheap as possible.

A heavy guhr can give a good catalyst, but a light guhr will give a better one. Some guhrs are heavy because the total composition is heavy, whereas others are heavy because, notwithstanding the fact that they contain good diatoms, up to 30 % sand is mixed ~~with the guhr. Dr Reulen suggested that we should send~~ about 10 l of various types of Kieselguhr available in the U.S. to Ruhrchemie to be investigated there.

10. Adjusters and measuring tanks.

At Holten the adjusters are tanks of 32 m3 each, into which the 3 solutions of magnesium, thorium and Co nitrate are run to obtain a final solution having the right concentration of 40 g Co/l. It is not implicit to adjust this concentration to exactly 40 g. In that case, however, one should know the exact concentration of the solution before using it for precipitating the catalyst in order to adjust the amount of Na_2CO_3 solution to be added. It facilitates, however, the operation if always the same amount and concentration of Na_2CO_3 solution can be used, for which reason the nitrate solutions are adjusted to an exact concentration of 40 g Co per litre.

Five such tanks are available at Holten, four of which being made of iron, lined with acid-proof brick, and one having rubber coating.

The solution in these adjusting tanks, still contains some free acid, e.g. 10 - 5 ~~20~~ g/l. This is due to the fact that an excess of acid is necessary to dissolve thorium. Magnesium can be dissolved with the theoretical amount of acid. From these adjusters the solution is pumped via a heater into tanks in which the solution is heated to exactly 60°C by means of indirect steam, as the concentration has to be kept entirely constant during this heating, and then run into measuring tanks. Measuring is done at exactly 60°C. This temperature itself is not important, but a certain temperature should be adhered to rigidly, in order to measure always the same amount of same specific gravity. As, after the measuring, dilution of the solution is immaterial, it is further heated with direct very pure steam - which is specially purified over filters - to 100 ~~98~~°C and then run off into the precipitation tanks.

11. Preparation of sodium carbonate solution.

This is done in the same kind of dissolving tank as used for dissolving Co in HNO_3. Calcined Na_2CO_3

and water are added into this tank and stirred while the dissolving procedure is going on. The solution should be made to an exact concentration of 103 - 104 g Na_2CO_3 per litre. Water for dissolving is again taken from the second part of the wash water used for washing the final catalyst after its precipitation on Kieselguhr.

12. Precipitation of catalyst.

Co, Th and Mg are precipitated as carbonates on Kieselguhr. Sodium carbonate solution is, therefore, heated in a tank to 60°C and then measured at exactly this temperature for the same reason as explained for the nitrate solutions. After being measured, the carbonate solution is run off into the precipitation tank, where it is heated further to ~~almost~~ its boiling point by indirect and direct specially purified steam before addition of the hot, ~~almost~~ boiling, solution of the nitrates. These high temperatures must be adhered to closely, as 10°C lower temperature will result in much inferior catalysts being obtained. As mentioned under 11, the sodium carbonate solution should contain~~s~~ 103 - 104 g water-free Na_2CO_3 per litre. During the precipitation step the contents of the precipitation tank are stirred vigorously. After addition of the nitrate solution, which is done very quickly, e.g. in 1 - 1.5 minutes, stirring is continued for 30 seconds longer and thereafter Kieselguhr added. This latter addition takes 80 - 90 seconds. Again stirring is continued for 30 seconds longer, and then filter so quickly as possible ~~the total contents of a precipitating tank being then pumped quickly via a screener to the filter presses. The reason for the screener is to remove any large undesired particles which may have been added with the Kieselguhr. Size of screen 10 mm.~~

After precipitation, the mother liquor will contain about 2 g Na_2CO_3, 6 - 7 g $NaHCO_3$ + {$Mg(HCO_3)_2$ per litre ~~titrates as bicarbo~~nate) and ~~70~~ 25-30 g $NaNO_3$ per litre.

There are sets of 4 precipitating tanks at Holten. One floor above the precipitating tanks are sets of 4 measuring tanks for the nitrate solution, 4 measuring tanks for the sodium carbonate solution and further 4 hoppers for the Kieselguhr, arranged as shown in figure 15, Annex A.

Into the precipitating tanks are run per charge:

a. 750 l nitrate solution, containing 31 kg Co;

b. 750 l Na_2CO_3 solution;

c. 62 kg Kieselguhr.

Belonging to a set of four precipitation tanks are ~~four~~ / eight filter presses for filtering these solutions, each filter press having a capacity of 2 precipitating tank charges containing 62 kg Co. Each filter press is able to handle 18 filter press charges or 18 x 62 kg Co per day. In all there are 1~~2~~0 filter presses at Holten, ~~6~~ 4 of which are in use.

After filtration the filter cake, having a thickness of 22 - 25 mm (this depends on the Kieselguhr, as some Kieselguhrs allow a thicker cake) is washed with ~~8~~-~~9~~ 5 m3 distilled water. This water should be as pure as possible and only contain the least possible amount of salts, as otherwise the activity of the catalyst will be impaired. The first part of this water is added to the mother liquor, consisting of sodium nitrate solution, and dumped. The second part is used for dissolving sodium carbonate, or used as wash water for the Fe-Th filter cake. However, at Holten this latter part can also be used for the first washing of the next filter press charge. The most efficient procedure of washing seems to be washing alternatively backwards and forwards, in which way the total quantity could be reduced to 130 ~~-~~ to 160 tons water per ton Co. dringend abzuraten

Filtering and washing should be done quickly, as otherwise the $NaNO_3$ will attack the ~~Kieselguhr,~~ contact,

Washing is done with hot water having a temperature of over 85°C, but not above 95 - 100°C. This washing takes about 25 minutes with new filtering cloth and about 35 minutes with old cloth.

The Na[illegible] concentration in the washed filter cake amounts to 0.0~~2~~3 % by weight, with a maximum of 0.06 % by weight, ~~or so~~. This amount should be kept as low as possible.

In this step 20 % MgO is lost; for instance, if the charge to the precipitating tank ~~should~~ contains 15 g MgO per 100 g Co, then the precipitated washed catalyst would only contain 12 - 13 g MgO per same quantity of Co.

The filter presses used now are so-called "Kammer filter presses"; formerly so-called "Rahmen filter presses" were in use. The first-mentioned ones, however, work much faster.

~~The final cake, after washing, still~~ contains about 76 % water.

13. Addition of dust.

After dropping the filter cake on the mixer beneath the filter press, dust (obtained further on in the process when granulating the catalyst) is added with so much water that the mixture of filter cake, dust and water is easily pumpable. About 30 - 40 - 45 %

(at present at Holten 38 %) on total catalyst to be dried is added as dust.

It has been found that the catalyst becomes harder when dust is added.

Formerly dust and water were added separately to the filter cake. At present dust and water are first mixed together, the slurry being added to the filter cake. After this addition, the mixture of filter cake, dust and water contains about 83 % water.

14. Further filtration and extruding of catalyst.

The above mixture is then pumped to a rotating vacuum filter working under a vacuum of 60 cm Hg, by which the amount of water is reduced to about ~~65~~ %. On this filter the catalyst is again washed with hot distilled water. Depending on the Co and $NaNO_3$ content the recovered water is either used for making the dust slurry mentioned above or run off into the general precipitating tank for the recovery of Co. 7-

The catalyst cake, after being scraped off the rotating vacuum filter, drops onto a kind of extruding machine, which presses the wet cake having a temperature of about 40°C through 6 mm holes. A cross-sectional sketch of this extruding machine is given in figure 16, Annex A.

The four blades A, B, C and D rotate in such a way that the catalyst mass is pressed through the holes. The clearance between each of the blades and the bottom plate with holes is 2 mm.

15. Drying of catalyst.

The driers used at Holten are not specially designed for this purpose, but bought as a normally available type. They consist of about 22 slowly rotating horizontal discs having a radius of about 2 - 3 ~~mm~~ m, each of which consists of segments and each having a scraper which scrapes the catalyst from a segment onto the corresponding segment of the disc just beneath it. Hot air is blown over this catalyst. This air circulates and is heated with 18 atm. steam through steam coils arranged in the heater alongside the walls. Fresh air enters the drier at the bottom after being preheated with 8 atm. steam. This is the expanded steam obtained from the 18 atm. steam used in the coils just mentioned. Wet air is removed from the drier at the top by means of a blower. The temperature of the air in contact with the almost dried catalyst should not be above 110°C ~~and not be~~ higher than ~~160°C~~ 120-130°C when in contact with the wet catalyst. Otherwise ~~the structure~~ of ~~the Kieselguhr [illegible] be harmed~~ (see fig. 17, Annex A).

The catalyst leaving the drier contains about 10 % of water.

The air leaving the drier is washed by water for dust recovery in a tower having trays with holes. This water is then passed through a filter press under its own pressure and the filtered water returned to the wash column by means of a pump. The recovered dust has been exposed to too high a temperature and is, therefore, unsuitable as such for the manufacture of catalyst. It is returned to the dissolving tanks for spent catalyst (see fig. 17, Annex A).

The total time of drying is about 2 hours. Capacity of the drier is about 5 tons of final catalyst per day. As about 30 % of the total dried catalyst is returned as dust, the actual amount of catalyst passing through this drier is, therefore, 30 % more.

Lately Holten ~~have started~~ intends to use driers which do not have a scraper for removing the catalyst from the disc segments, but which make these segments turn slightly at a certain point to let the catalyst drop onto the corresponding lower segment. It was said that this kind of drier causes less dust formation. For the same reason they intend using a continuous belt drier, in which a belt slowly moves downward through the drier, leaving the catalyst in its place on the belt during the entire time of its presence in the drier.

16. Screening and granulation.

The catalyst leaving each of the four driers is moved by a horizontal belt conveyor to a vertical bucket conveyor (elevator) which drops the catalyst onto vibrators. There are two bucket conveyors or elevators at Holten, each dropping the catalyst onto two vibrator sets, each vibrator set consisting of:

first vibrator,
granulator,
second vibrator,
third vibrator.

(See fig. 18, Annex A).

The first vibrator separates the catalyst by means of 2 vibrating screens, viz. a ~~2.5~~ 3.5 x 3.5 screen and a 1 x 3 screen, into three different sizes, viz. too large size, good size (1 - 3 mm) and dust (everything passing the 1 x 3 screen). The oversize particles not passing the ~~2.5~~ 3.5 x 3.5 screen are fed to the granulator, which consists of a screen and a slowly rotating arm pressing the oversize particles through the screen. The material leaving the granulator drops onto the second vibrator having three screens, viz. from top to bottom:

a ~~2~~3.5 x 3.5 screen
a 2.5 x 2.5 screen and
a 1 x 3 screen.

The particles not passing the top screen are returned via the elevator to the first vibrator. The particles not passing the second screen are fed to the third vibrator, as well as the particles not passing the third screen. Everything passing the latter screen is dust and drops into the dust collector. The third vibrator consists of two screens, viz. a 2.5 x 2.5 and a 1 x 3 screen. This vibrator serves for removing any dust left in the good-size particles and, therefore, receives the good particles from the first vibrator (1 x 3 screen) and the second vibrator (2.5 x 2.5 and 1 x 3 screen), giving, therefore, two different-sized particles, which is necessary, as some licensees ask for smaller and some for larger particles.

The vibrators are enclosed and work under a slight vacuum in order to prevent dust from escaping into the atmosphere.

Catalyst of the desired size is put into paper bags, each containing 30 kg catalyst. This catalyst is called "green catalyst", which contains about 22-24% of Co and 7-10% of water.

17. Hereafter the catalyst is reduced with hydrogen which is previously heated to about 450 - 460°C.

Ruhrchemie use mixed gas of their ammonia plant for this reduction step instead of pure hydrogen.

This gas is kept in circulation. After passing through the catalyst to be reduced, it is freed from CO_2 and H_2O in various units and then returned via a heater to the reduction chambers containing the "green" catalyst (see Annex A, figs 6 and 7).

The reduction plant consists of the following parts:

a. reduction chamber,
b. conversion of CO_2,
c. spray cooler with separator,
d. Junker's cooler,
e. gasometer,
f. blower,
g. cooler,
h. blower,
i. cooler,
j. ammonia cooler,
k. Silica gel drier,
l. gas heater.

a. A sketch of the reduction chamber is shown in fig. 20, Annex A.

By lifting the top part, the inner basket, having a height of 35 cm, can be filled with catalyst. At Holten the depth of such a catalyst layer does not exceed 20 - 25 cm. About 8 paper bags or 240 kg catalyst are filled each time in each chamber. When reducing, the hot hydrogen passes through the "green" catalyst from top to bottom, heating it to 380 - 4~~5~~70°C. The following conditions are absolutely necessary for obtaining an active catalyst:

1. a thin layer of "green" catalyst;
2. high velocity of the hydrogen;
3. low vapour pressure of H_2O and CO_2, say, below 0.1 g H_2O per m3 circulating gas;
4. constancy in conditions, e.g. temperature, H_2 velocity and purity of H_2.

The catalyst is not sensitive to H_2O and CO_2 at room temperature, but very sensitive at higher temperatures.

If the vapour pressure of H_2O and CO_2 should be too high, the temperature has to be increased in order to obtain a good reduction.

However, this increased temperature, say, above 450°C, produces a considerably less active catalyst. One may expect, therefore, a still better catalyst than obtained at the moment by reducing at still lower temperatures. Holten have succeeded in reducing even at 300 - 320°C. However, the time of reduction is then about four times longer than at 380°C.

It is very difficult or even impossible to measure the actual temperature within the catalyst.

The difference in gas temperature between the inlet and outlet of the catalyst bed is about 200°C when starting the reduction. This difference decreases gradually and is usually about 80°C towards the end of the reduction. However, this temperature difference is not a guide for the time of reduction.

The amount of hydrogen used at Holten is 1200 m3/h gas ($3H_2 + N_2$ + impurities) per m2 catalyst surface. This quantity cannot be increased much, as otherwise the catalyst will start swimming. To prevent this, a set of distributing vanes, having about 10 x 10 cm squares and a height of about 10 cm, is attached to the top cover of the chamber. When this cover is closed the distributor is pressed about one inch into the catalyst bed.

The figure of 1200 m3 mixed gas/hour/m2 does not mean that with pure hydrogen one could use 900 m3/hour/m2, as a certain partial pressure of water should not be exceeded and enough gas has to be passed through to dissipate the heat of methane formation.

It is said that with pure hydrogen the reduction temperature can be reduced somewhat.

At Holten there are six chambers, each of which is connected to one hydrogen header. The total quantity of gas passing through the chambers, which means the total quantity of gas in circulation, is 10,000 m3/h. Every 20 minutes a chamber filled with catalyst is being connected to the hydrogen cycle to start the reduction. This reduction takes one hour, for which reason all the time 3 chambers will be connected to the hydrogen cycle and the amount of 10,000 m3 just mentioned is, therefore, passing through 3 chambers all the time. In order not to increase the percentage of impurities above a certain limit about 950 - 1450 m3 gas per hour is continuously blown off and 1000 - 1500 m3/h fresh $H_2 + N_2$ added. The ~~six~~ 12 chambers together can reduce six synthesis converter charges per day. Cross-sectional surface of one reducing chamber is 1.4 m2.

During this reduction a small amount of dust is formed, which is removed in the cooling stage mentioned sub b.

After reduction is finished (this time is known by experience and not controlled by any analysis) hydrogen is replaced by N_2. Then connections from and to the chamber are removed, the chamber turned upside down and connected to a much larger container, which can be moved backwards and forwards under each of the six reducing chambers. This latter container is filled with nitrogen and reduced catalyst is dropped into it. It can hold 15 - 17 reducing chamber charges, i.e. an amount equivalent to 15 - 17 x 240 kg "green" catalyst. Smaller containers are also in use, having a capacity of 4 - 5 reducing chamber charges.

All work in this reducing plant is manual. Time needed for the various operations in the reduction step in a most mechanized plant is as follows:

60 minutes for reduction;

10 minutes for replacing H_2 by N_2, disconnecting chamber and turning it upside down;

5 minutes for emptying the chamber;

10 minutes for turning chambers, filling, reconnecting to cycle and purging with nitrogen.

In a new catalyst plant charging, discharging, etc. will all be done automatically, which will also reduce the time for the total cycle.

b. Conversion of CO_2.

As mentioned under a, it is imperative to keep conditions constant during the reduction step in order not to impair the activity of the catalyst. However, this has not been entirely possible as part of the CO_2 removed from the green catalyst (carbonate) stayed in circulation and was converted to CH_4 when coming again into contact with the already partly reduced catalyst. This caused a continuous variation in CO_2 and CH_4 content of the recirculating gas. Moreover, everything that has been said with respect to a necessary low vapour pressure of the water also holds good for CO_2. Removal of CO_2 after the reduction chamber, therefore, was expected to give a better catalyst. Holten are afraid that this cannot be done, however, by caustic wash, as the chances are that a small part of the caustic may be carried through to the catalyst. They have, therefore, just started to reduce the CO_2 to CH_4 over a catalyst right after the reduction step. This can be done at 180 - 250°C, when no or hardly any water is present. However, with the actual amount of water present, viz. 40 - 50 g/m3, in the gas after the reduction chamber (e.g. reaction water and moisture present in the green catalyst) a temperature of 350 - 400°C is necessary. This is somewhat higher than the average temperature of the gas when leaving the reduction chambers, for which reason a special heater is now being installed. Without this heater only 40 - 50 % of the CO_2 which is present in the gas after the reduction chamber to an amount of 1.7 g/m3 can be converted, as the gas temperature is only 250 - 300°C. As catalyst for this $CO_2 \longrightarrow CH_4$ reaction Holten use their ~~synthesis catalyst, which they expect will last for~~ a long time.

c. Spray cooler.

The spray cooler reduces the temperature of the gas leaving the reduction chambers from 300 - 400°C to about 40°C, at the same time removing any dust carried along.

This latter amount is very small and dust which remains in the tower is only removed from it twice a year (see fig. 23, Annex A).

d. The Junker's cooler is a tubular indirect water cooler, the temperature, after this cooler, therefore, depending on cooling water temperatures and being, say, about 25 - 30°C.

f, g, h, i. There is no reason why the 2 blowers + 2 coolers could not be reduced to 1 blower + 1 cooler. Pressure after the second blower: 4000 - 5000 mm water.

It is worth mentioning that the use of Roots blowers cannot be recommended, as such blowers give impulses to the gas flow, and most important is that the gas should pass smoothly over the catalyst during its reduction.

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j. The ammonia cooler brings the gas temperature down to -10°C. -12°C ~~This~~ cooler has a capacity of 150,000 kcal/h, about -10°C, the compressor using 80 hp, and is guaranteed to reduce the water content to below 5 g/m3 gas. Actually at Holten about 2 g H_2O/m3 or less is reached.

The equipment consists of one heat exchanger (recuperator) and 2 NH_3 coolers in parallel.

k. The silica gel plants at Holten consist of two driers, operating alternatively. Each drier has 2 layers of silica gel and switching over to the other drier is done long before the bottom layer is saturated with water. The gas entering these driers at the top contains about 2 g H_2O/m3 and leaves the drier with 0.04 - 0.05 g H_2O/m3.
0.04 - 0.05

Regeneration is carried out with hot hydrogen in circulation, which is heated with steam to 140°C. After regeneration is finished, the silica gel is cooled by hydrogen in circulation, this being itself cooled indirectly by water. The cycle is: one hour absorption, one hour regeneration.

When starting operation, Holten used gel driers constructed by the Silica Corporation in the U.S.A. At that time they did not have an ammonia cooling. The gas entering this drier, therefore, contained about 25 g $H_2O/m3$, leaving the drier with about 0.8 g $H_2O/m3$. As the gel cannot stand such large amounts of water present in the fresh feed a gas volume of about 3 - 4 times the amount of fresh feed was kept in circulation to dilute the fresh feed with dried gas. Regeneration according to the Silica Corporation's method was carried out by the hot gas itself, after leaving the reduction chambers described under a and having a temperature of about 250 - 300°C. After the gas left the gel unit to be dried, its temperature was about 100°C. It was then cooled and passed through the gel absorbing unit (see Annex A, fig. 24).

This method of drying did not prove to be very successful, as

1. the driers had too much resistance for a fresh gas rate of 10,000 m3 gas/h. With normal blowers one cannot attain much more than 6 m H_2O. Increasing this pressure, considerably increases the power consumption, e.g.

   6 m H_2O : 250 kW,
   8 m " : 350 ".

2. Some dust from the reducing containers accumulated on the gel. Holten installed a dust catcher, but owing to the small amount of dust and the particles probably being electrically charged this did not work well.

As a gel drying preceded by NH_3 cooling was considered to be considerably less expensive, an NH_3 cooling system was installed, at the same time replacing the gel unit just described by gel driers from Gebr. Hermann, Köln. Now the results mentioned in the first paragraph of this point <u>k</u> are being obtained.

1. Gas heater.

The gas heater consists of a tubular bundle through which hydrogen passes from top to bottom and is heated by hot flue gases obtained by burning rest gas with air. Also in this case the tubular bundle consists of two parts which allow independent expansion of the tubes heated by the flue gas entering the bundle (vide Chapter II). (See Annex A, fig. 19).

18. <u>Cooling</u> of reduced catalyst and saturation with CO_2 or oil. As mentioned before, the reduced catalyst is dropped hot into small or larger containers, holding either 4 - 5 or 15 - 17 reducing chamber charges. After being filled, these containers are cooled, which is done outside the reduction part of the plant with circulating N_2 (see Annex A, fig. 7a). Time for cooling of a large container: 5 - 8 hours; for a smaller container: about 2 hours. When a temperature below 40 - 45°C is reached the catalyst is saturated and impregnated with CO_2 by feeding CO_2 through the catalyst from bottom to top. This saturation is continued until the gas leaving the top of the catalyst container shows a CO_2 content above 98 %. 120 kg CO_2 is used for a large container. This step takes about 100minutes.

The circulating N_2 is cooled itself indirectly by water. The cross-sectional form of the tubes of this cooler is stream-lined. The tubes are made of aluminium and have a diameter, square to the stream-line direction, of about 1". Wall thickness 0.3 - 0.6 mm. These coolers are made by Rudolf Otto Meyer, Hamburg, and are said to be very cheap, viz. about half the price of normal tube coolers. They are also used by the German Navy and are called "aerodynamic coolers".

Instead of CO_2 also oil can be used; for instance, a catalyst charge shipped to Japan had been impregnated with oil. Although this latter procedure apparently does not harm the overall activity of the catalyst, its starting activity is somewhat lower than in case of CO_2 impregnation.

If the catalyst has to be transported over a long distance solid CO_2 is put on top of it after the CO_2 impregnation is finished.

<u>19</u>. Transport of catalyst to licensees. For transporting catalyst to licensees two methods are used:

1. two large catalyst containers on a railroad car, each container having a dead weight of 5650 kg. One fresh catalyst charge weighs 3000 - 3250 kg. After use the spent catalyst might weigh up to 5000 kg, owing to paraffin absorbed in the catalyst. For this reason the Holten cranes have been amply dimensioned at 15 - 17 tons.

2. Eight small containers on a railroad car, each weighing empty 1470 kg and each having a capacity of 800 kg catalyst. Therefore, four such containers just have enough capacity for one oven charge. The form of these containers is shown on figure 21, Annex A. Dimensions are 1570 mm long, 1420 mm wide and 2135 mm high; total volume 3500 litres; net volume 2500 litres. Lately these containers have been transported to the various licensees in upside down position, in order to facilitate filling the synthesis converters and making it possible to transport the containers on rails on top of the ovens, allowing a lighter construction of the synthesis building. See fig. 22, Annex A.

For sketch of transport cars see figure 21, Annex A.

20. Some remarks on equipment installed at Holten's catalyst plant.

It may have been noticed that for all filtering steps, except one, filter presses are used. Ruhrchemie stated in this connection that when designing the plant this type of press has been chosen on purpose, as it is very flexible and reliable for all types of precipitates, independent of crystal size, and furthermore ensures effective washing of the filter cake.

Once the conditions for a certain precipitation step are known and rigidly adhered to, one can advantageously apply continuous filters, thereby reducing materially the cost of upkeep and labour.

Regarding the material for the equipment to be used in the catalyst plant, the following can be said.

Iron can be used throughout the plant when no free acid is present.

Parts coming into contact with neutral catalyst, whether dry or wet, should not contain or be made of: copper, bronze, zinc, tin, aluminium or lead.

Whenever HNO_3 is present it is necessary to use either iron with acid-proof lining (bricks, rubber), or Cr-Ni steels, or alloys such as ascaloy or sichromal (DEUTRO 16-S made by Vereinigte Stahlwerke Thyssen, Düsseldorf, or V_{17} F.E. made by Krupp. Both these metals contain a small amount of Ti and can be welded without being annealed afterwards).

For the final catalyst precipitation V_2A is used. It is important for better cleaning that these containers have a smooth surface, for which reason sichromal, which, moreover, oxidizes quicker, is less desirable.

All pumps can be of normal construction. They should run at moderate speed to avoid excessive wear; for more viscous liquids open vanes should be applied. In case of acid-containing liquids, Cr-Ni or Cr-steel or stoneware is to be used. The latter material is not applied at Holten.

As mentioned in the foregoing description filter presses for acid-containing liquid are made of wood, for which pitch pine is specially recommended.

NaF is pumped through iron pipes.

In the purification steps mostly wooden tanks are used.

Iron is used in the reduction plant throughout.

As packing material rubber is mainly used, except at hot places, where asbestos packing is applied.

The following names of manufacturers may be mentioned:

Vacuum filter:	Maschinenfabrik Buckau R. Wolf, Magdeburg.
Extractor:	Büttner Werke, Uerdingen ("Spezial Aufgabe Apparat für Pastenförmige Produkte").
Drier:	Büttner Werke, Uerdingen.
Vibrator:	Flämrich, Recklinghausen.
Reduction step cooler:	Junker's Cooler, Dessau.
Nitrogen cooler:	Rudolf Otto Meyer, Hamburg.
Hydrogen heater:	Rekuperator, Düsseldorf.
Heater for heating the $Co(NO_3)_2$ solution before removing Fe, Al, etc.:	[illegible] Müller [illegible] ~~Fritz Scheibler.~~ Schmidding Köln

<u>Capital costs and utility requirements for a catalyst plant for manufacturing Co-Mg catalysts, sufficient for 200,000 tons of liquid product per year.</u>

This catalyst plant should have a capacity for the re-generation of 1½ converter fillings per 24 hours; the capital cost for such a plant built in Germany under the present circumstances would amount to RM 2,100,000.

This includes buildings and apparatuses, cooling water supply, purification of wash water, all electrical equipment, settling pits, etc.

~~The costs for buildings amount to 25 - 30 %,~~ which buildings are necessary in Germany on account of the possibility of freezing.

When built in the South of the U.S.A. it might be possible to reduce the capital investment by omitting or simplifying the buildings.

The above plant can normally re-work 1.3 tons of Cobalt with a maximum of 1.6 tons of Cobalt per 24 hours.

The utility requirements were stated to be as follows:

Condensed water, 200 tons/ton Cobalt; this quantity is sufficient also for making solutions, etc.

If the costs for preparation of condensed water should be extremely high, it might be possible to reduce the above-mentioned quantity to 130 - 160 tons, replacing the balance by normal tap-water.

The latter should then be used for the washing of the Kieselguhr, diluting of nitric acid, etc.

Apart from these quantities make-up for cooling water and a certain quantity for rinsing water are necessary.

It was mentioned in this respect that the condensed water-distilling plant at Lützkensdorf is dimensioned for a quantity of 288 tons/24 hours for regenerating 3 tons catalyst per 24 hours. This must be considered to be a bottom figure.

The cooling water circulation for regenerating 1½ tons of Co is to be set at somewhat more than 200 tons per hour; the returning cooling water from the refrigerating plant is taken at 30 - 40°.

If cooling water in large quantities and of sufficiently low temperature is available (e.g. from a river), the quantity of circulation water can be reduced considerably.

The steam consumption will be from 4 - 7 tons per hour for regenerating 1½ tons of Co/24 hours.

Regarding the electrical facilities the following figures were given:

The total rated capacity of the electrical motors in a plant for re-generating 1½ tons of Co/24 hours is about 780 kW. The actual consumption will be about 25 % of this figure, i.e. 200 kW.

The total quantity of Co tied up in the catalyst plant of the above-mentioned capacity, may be estimated at 30 tons.

This figure may be considered as ample, but when such a quantity is available, a smooth running of the catalyst plant is facilitated.

CHAPTER IV.

MANUFACTURE OF CATALYST FOR ORGANIC SULPHUR REMOVAL.

This catalyst is prepared by mixing lux mass with sodium carbonate.

The lux mass is stored in the open and contains 50-60% water, and also some alkaline (7%), calculated as sodium carbonate, partly consisting of NaOH, partly of Na_2CO_3.

It is mixed with the soda in a so-called counter-current mixer (Esch Hochleistungsgegenstrommischer, Esch Werke, Duisburg). This is a cylindrical mixer of about 2 m dia. with a vertical spindle, with a planetary system of scrapers revolving around it.

In this mixer 600 kg of lux mass containing 50% of water, 100 kg of dry calcinated sodium carbonate and about 220 kg dust (see below) are mixed at a rate of 5-7 charges per 8 hours. So much water is necessary that the mass is just sufficiently plastic. If the lux mass contains less than 7% alkali, a corresponding quantity of Na_2CO_3 is added above the quantity of 100 kg mentioned before.

The lux mass and the soda are mixed for about 1/4 hour, after which about 1/2 the quantity of dust is added, followed by 20 minutes' mixing. Then the remaining dust is added and the mixing continued for 5 minutes, after which the mass is dropped through the bottom.

After mixing, the mass is dropped by an "Entleerungsklappe" and fed by hand to a so-called "Passier" sieve, consisting of a horizontal plate with holes varying in diameter from 3/8-5/8 inch, drilled in 3 of the 4 quadrants. Arms revolving on a vertical spindle push the mass through these holes, from which it drops onto the revolving blades of a hot air drier.

It is important that the mixing should be well timed, to attain the desired plasticity of the mass, which hardens rather quickly by cooling below 32°.

Delay in passing through the "Passier" sieve might result in breakage of the arms; it has been found, however, that the mixing time does not influence the quality of the product. An extruder such as is used for the manufacture of synthesis catalyst would be unsuitable in this case.

The drier (Büttner Werke, Uerdingen), of the same construction as used in the synthesis catalyst plant, has a diameter of 6 m, the inside diameter of the vanes being 3 m. The drier has 22 sets of vanes, spaced at a vertical distance of 200 mm.

The air for the drier is pre-heated in a tubular heater with steam of 18 atm., the heating coils in the drier getting steam at 8 atm. The temperature of the air in the drier is about 100°, with a maximum of 120°; a higher temperature would result in too much splitting up of the mass. The latter enters the drier with about 35% water and leaves it with 3-5%. After leaving the hot air drier, the product is taken up by a bucket conveyor and fed to a vibrating sieve, which separates:

a) parts over 15 mm
b) product from 10-15 mm
c) parts under 10 mm (dust).

The oversize product is passed through a breaker and sieved in a second vibrator. The oversize from this apparatus is transported back to the first vibrator.

All parts under 10 mm are taken up by a conveyor and used as stated before, together with the dust, which is collected by a special vacuum system; the dust-catching bags are emptied periodically by releasing the vacuum.

The capacity of the hot air drier was stated to be 15 tons/24 hours. (For synthesis catalyst driers the capacity was given at 5 tons). It is considered that this type of drier could be replaced successfully by a belt-type drier, where the material stays on a belt and is not dropped periodically onto the lower set of vanes.

The above-mentioned size for the product of 10-15 mm is used at present by way of trial; normally sulphur catalyst of 5-15 mm has been used. Also experiments with 5-10 and 10-20 mm are being carried out.

The chemical analyses of lux mass and sodium carbonate are available at Holten.

CHAPTER V.

CYCLE OF FILLING AND DISCHARGING A SYNTHESIS CONVERTER.

When filling a converter, a large or small catalyst container is put on top of such a converter in which air has been replaced by CO_2 by introducing this gas at the bottom and further by putting a special frame on top of the oven and blowing CO_2 from cylinders through this frame. The catalyst, saturated with CO_2, is then dropped from the container into the oven, which has to be done carefully in order to get an even distribution of catalyst over the converter cross section. During the filling procedure a small stream of CO_2 is blown continuously through the frame on top of the oven.

After the converter has been filled, the oven is closed. As the top cover is concave, leaving an atmosphere of air above the catalyst, nitrogen or CO_2 is blown under this cover over the catalyst to replace this air.

Filling and closing a converter takes about 3 hours.

The converter is then heated up by blowing 18 atm. steam into the water-circulating system. This takes ~~about 2 - 3 hours and is continued until a steam pressure~~ of 5 atm. is reached. Then synthesis gas - preferably gas from a first-stage converter - is passed over the catalyst in order to determine whether or not reaction will start, which is shown by the CO_2 recorder. If so, then no further heating is done. If not, heating is continued while synthesis gas is passing through, until reaction starts. This is generally the case when a steam pressure of 5 - 6 atm. is reached.

The initial gas rate is 600 - 700 m3/h, which is raised gradually to 1400 m3/h. When starting on gas from a first-stage converter, after about two - three days the switch-over to fresh gas is made or the new converter is left in the second stage for more than half of its lifetime, as in this case the catalyst will be more protected, mainly from sulphur. Figures given were about 2500 hours in the second stage and the rest of its lifetime in the first stage.

It is also possible to start a converter on fresh gas; however, in that case the initial gas rate should not be over 600 m3/h, which furthermore should be very slowly increased. This quantity is limited by the capacity of the steam back-pressure regulator. in Holten

Conversion in either stage is controlled by the CO_2 content, as fresh gas entering the first stage has a practically constant percentage of CO_2 (about 13.4 % at Holten). When working on a 75 % contraction in the first stage, gas leaving this stage would contain about 55 % CO_2. At 57 % contraction, which is normal, the CO_2 content would be about 35 - 36 %. 57 % contraction means a conversion of CO of about 70 %.

Normally operation is as follows. After starting, as explained above, with a gas rate of 600 - 700 ~~m3/hour, which is increased gradually, a fixed gas rate~~ of about 1200 to 1300 m3/h is maintained. By controlling the steam pressure the temperature is regulated in such a way as to obtain a certain conversion of CO. By gradually raising the temperature up to, say, 200°C, this CO conversion is practically kept constant. Further increase in temperature is not advantageous owing to increasing methane formation. Therefore, once a certain maximum temperature has been reached the gas quantity would have to be gradually reduced in order to maintain the same CO conversion.

However, in actual practice the catalyst is regenerated before this maximum is reached, e.g. after about 1000 hours' operation, by which time the operating temperature has been increased to about 195°C. After this regeneration (hydrogenation) which will be explained below, it is possible to obtain again the same CO conversion as before with the same gas rate, but at a lower temperature, for instance 190°C. Again this temperature is gradually increased to about 200°C in order to maintain the same CO conversion. This will then take about 800 hours, at about which point the catalyst will be regenerated a second time. Soon after this second hydrogenation it will be necessary gradually to reduce the gas rate, maintaining the temperature at a maximum of 203 - 205°C. The gas rate is then lowered very slowly to a minimum of about 800 m3/hour over a relatively long period of time, during which one or two more regenerations will be carried out. If the CO conversion at this final gas rate and a temperature of 203 - 205°C drops below 55 - 60 % in the first stage, usually such converter is taken off the line.

Dwg 2M 106/16 ~~Graph N° 1 in annex E~~ shows the actual variation of gas rate, contraction and "Leistung" with the time during the entire lifetime of two catalyst fillings. During this period 4 regenerations were carried out. It is interesting to see that the "Leistung" before the first regeneration was exactly the same for the two converters. After this regeneration one converter showed a slightly better "Leistung" than the other one. One will furthermore notice the drop in operating temperature after each regeneration.

We were told that both these converters were kept for more than the usual length of time in the first stage.

The hydrogen to be used for these hydrogenations or regenerations should be free from CO as much as possible, i.e. should contain less than, say, 0.1 % CO. The CO_2 content should preferably not be higher than 1 to 2 %. This hydrogen is kept in circulation at a rate of about 1500 m3 per hour per converter. It passes the converters in the same direction as synthesis gas, i.e. from top to bottom, is then cooled down to separate any liquid products and returned by a blower to the converter.

Part of this circulation gas is continuously blown off in order not to increase the methane content above a certain percentage and fresh hydrogen continuously supplied to the cycle at a rate of 300 - 400 m3/h for two converters. Analyses for methane before and after the converter show whether the regeneration (hydrogenation) is finished.

After a catalyst is taken off the line it is once more hydrogenated to lower the wax content before transporting it to the catalyst plant. In the beginning Holten used pure hydrogen for this latter hydrogenation also, but lately they have started using synthesis gas with the additional purpose of trying to kill the catalyst at higher temperatures and furthermore because synthesis gas is cheaper. As synthesis gas usually gas from the first stage is taken, but fresh gas can also be used for this purpose. When hydrogenating with pure hydrogen no increase in temperature is noticed. However, with synthesis gas the catalyst is still active enough to give a rise in temperature. The steam pressure is then kept at about 19 atm. The time for this last dewaxing step is about 24 hours.

When starting to use synthesis gas instead of hydrogen for dewaxing, Holten apparently did not have any more pure Co-Th catalysts in operation. We were told, however, that with Co-Th catalyst they would prefer to use hydrogen mixed with some synthesis gas, as dewaxing of this catalyst is more difficult than of catalysts containing Mg.

The latter dewaxing and the regenerations mentioned above with pure hydrogen during the period of actual operation are carried out in order to free the catalyst as much as possible from accumulated paraffin, which is cracked at the normal operation temperature in the presence of hydrogen. In the case of normal hydrogenation with pure hydrogen about 3000 kg total products, of which about 1500 kg consists of CH_4, are obtained per converter. When dewaxing with synthesis gas just after taking a converter off the line, very probably more CH_4 and more total products are formed, firstly because this cracking is carried out at higher temperatures and secondly because CH_4 will be formed not only from the paraffin itself, but also from the CO of the synthesis gas. When using pure hydrogen for the last hydrogenation it is necessary to heat the catalyst with steam. An endeavour was made to preheat the hydrogen to 350°C, but this did not help at all.

In future Holten may apply extraction with certain gasoline fractions instead of regeneration with hydrogen. They consider extraction to be a better method of removing paraffin from the catalyst, but the best method of doing this, and what gasoline fractions should be used, has still to be investigated. It is realized, however, that in this case no Cobalt carbides, if formed during the synthesis operation, can be reduced, as is done apparently when regenerating with hydrogen.

After this last treatment with synthesis gas at higher temperatures is finished, the steam pressure is released very quickly to atmospheric or somewhat higher pressure, which will cool down the converter. Then a few preparations have to be made before the converter can be discharged, during which time the converter will cool down somewhat more. The gases within the converter are replaced by nitrogen or CO_2. An almost horizontal chain scraper is connected to the bottom part of the converter and an almost vertical bucket conveyor fitted in such a way that the catalyst, after leaving the first conveyor, is picked up and dumped into a catalyst container (see Annex A, figure [illegible]). Then the two bottom plates, on which the catalyst rests, are opened, which can be done from the outside.

In general the catalyst runs easily out of the converter. When most catalyst has been transported via the two conveyors into the catalyst container, the oven is further cleaned by poking and, if necessary, air blowing. In case the catalyst should not run out freely, the converter is completely closed again and again treated with synthesis gas at higher temperatures, as described above.

Air in the catalyst container should be entirely replaced by CO_2 before starting to fill it with spent catalyst. CO_2 is also blown over the conveyor during transport of the catalyst from converter to container. After being filled, the container is closed and brought to the catalyst plant.

Generally, spent catalyst is not stored; this is not on account of the catalyst itself, but only to limit the number of containers in circulation.

This catalyst still contains paraffin, viz.

when using Co-Th catalysts	15 - 35 %
for mixed catalysts	8 - 20 %.

An endeavour was made at the time to remove this paraffin from the catalyst in situ, which means in the converter itself, with steam. This did not meet with success, as a temperature of about 400°C is necessary and Ruhrbenzin's synthesis plant is not equipped for preheating the steam to this temperature. Therefore, steaming to remove paraffin was worked out separately and, when found to be possible, carried out in the catalyst plant before starting the dissolving, etc., procedure. Since using catalysts containing Mg, steaming of spent catalyst is not necessary any longer, as such catalysts usually do not contain more than 20 % paraffin, which remains in the Kieselguhr during the dissolving procedure. The catalyst is, therefore, now dropped from the containers into barrels, which are emptied directly into the dissolving tanks. All spent catalyst is tested on its paraffin content (this analysis takes about one hour), because steaming is still carried out when the paraffin content is over 25 %.

This steaming not only lowers the paraffin content of the catalyst, but also helps to kill the activity of the catalyst; as spent catalyst is of pyrophorous nature. Formerly all spent catalyst, even if the paraffin content was not too high, was entirely de-activated, losing thereby its pyrophorous nature. This latter treatment could be done with either steam or steam + air or air alone.

With Th catalyst one has to be very careful not to exceed certain temperatures when oxidizing the catalyst with air, as otherwise part of the thorium will become insoluble in nitric acid. Such temperatures are, when measured with a thermometer in the catalyst, 150 - 190°C. The actual catalyst temperature may be then as high as 400 - 500°C. Therefore, in such cases, oxidation - that is killing the activity - should be carried out slowly or by small additions of air or oxygen to nitrogen. Cobalt itself is not sensitive to these temperatures, although when going to still higher temperatures one apparently passes a range in which Cobalt can also be harmed.

It is also possible to oxidize with steam, in which cases the temperature may be considerably higher without affecting the dissolving properties of the thorium. However, this is more expensive and more difficult from a mechanical point of view. Nevertheless, when de-activating Th catalyst, Holten think that steam is to be preferred, as in that case it is not necessary to control the temperatures very closely.

The amount of gas which is circulated when oxidizing with air is 300 m3/h. When working with steam 1 - 1.5 tons per hour is required. Duration: 10 - 12 hours per oven charge when using air; 18 - 20 hours per oven charge when using steam.

An endeavour will be made to oxidize the spent catalyst, while still in the converter, by introducing small quantities of oxygen to steam.

Holten are installing new equipment for transporting the spent catalyst - which now no longer consists of pure Co-Th catalyst and, therefore, does not contain too much paraffin - directly from the converter to the dissolving tanks. In this case the spent catalyst will be dropped into a vessel of about 2 m3, into which

$Co(NO_3)_2$ solution also runs, equipped with a stirrer which mixes the spent catalyst vigorously with the nitrate solution and from which a pump takes suction, pumping this solution directly into the dissolving tanks, at the same time recirculating part of the liquid back into this vessel. This would save much time and labour if found to be a success.

Ruhrchemie's catalyst plant is able to rework about 6 - 8 converter charges per day. Ruhrbenzin's own consumption is not more than half an oven charge per day; therefore, it is considered to be a small plant and most of the spent catalyst they rework comes from their licensees.

There are apparently 3 catalyst plants at present in Germany, viz. one at Holten, one at Ruhland and one at Lützkendorf. Outside Germany this Fischer process is applied, for instance, by Kuhlmann, who also have their own catalyst plant.

CHAPTER VI.

Questions raised during the study of the process by Partners with answers by Dr Alberts.

November 1st 1938.

Several questions were discussed, which Dr Alberts answered as follows:

1. Throughput of ideal gas per ton Co per hour in first stage ?

This depends on the amount of inert gas.

a) At atmospheric pressure: 1300 m3 per hour total gas, including inerts. This is an average and remains the same whether more or less inerts are present. Production: 100 g liquid product + 12 g gasol per m3 ideal gas.

b) At higher pressures: the pressure can probably vary between 5 and 10 atm. At higher pressures the trend goes towards more paraffins and more saturated hydrocarbons. Therefore, at 5 atm. less paraffins will be produced and the power consumption will also be less than at 10 atm. From 10 - 15 atm. neither yield nor paraffin content vary (this means a variation of not more than 2 %). Above 15 atm. both yield and paraffin content drop appreciably.

Difference in yield and paraffin content between 7 and 10 atm. is very small.

At higher pressures more oxygen-containing products are formed and at still higher pressure the reaction goes more and more towards the methanol synthesis.

Note: Numbers omitted relate to questions which have been dealt with in other chapters.

Throughput in case of pressure synthesis is about 20% higher that at atmospheric pressure. Yield: 125-130 g liquid product + 7 g gasol per m3 ideal gas.

Note.

Figures at atmospheric pressure are actual plant data over long periods. Figures at higher pressures are data mostly from laboratory and pilot plant tests.

2 **Throughput per ton Co per hour in second stage ?**

Both at atmospheric and higher pressures the throughput in the second stage is about 10% more synthesis gas (not ideal gas) than in the first stage.

Yield at atmospheric pressure: 20 g liquid product + 3 g gasol per m3 ideal gas entering first stage.

Yield under pressure: 25 to 30 g liquid product + 3 g gasol per m3 ideal gas entering first stage.

Therefore, total yield:
atmospheric pressure: 100 + 20 = 120 g liquid product and 12 + 3 = 15 g gasol per m3 ideal gas;
under pressure: 125 to 130 + 25 to 30 = 150 to 160 g liquid product and 7 + 3 = 10 g gasol per m3 ideal gas.

3-4. With and without pressure 90 - 92% of the CO is ~~being converted. Difference in yield between the two~~ processes has to be explained by a larger or smaller production of methane.

Theoretical yield from 1 m3 ideal gas is 210 g per m3.

Holten use gas with about 15 - 17% inerts. The contraction in the first stage is about 60 - 65%, for 70 - 75% conversion of CO, whereas the contraction in the second stage is about 30 - 40% on the gas entering the second stage.

5. Total production in first stage ?

Atmospheric pressure: Catalyst life in both stages is about 4 months or 122 days. Throughput at Holten is about 1300 m3 total gas per ton Co per hour or about 1100 m3 ideal gas per ton Co per hour. Therefore, total production in first stage is 122 x 24 x 1100 x 100 = 322 tons liquid product per ton Co.

Pressure: Catalyst life 6 months, or 183 days. Total production, therefore, in first stage : 183 x 24 x 1100 x 125 x $\frac{12}{10}$ (20% more throughput) = 720 tons liquid product per ton Co.

6. Total production in second stage ?

This depends on the number of first-stage ovens connected to one second-stage oven. During its whole lifetime a catalyst remains in the stage in which it has been put originally. Generally 3 first-stage ovens are connected to 1 second-stage oven. Supposing that 1000 m3 total synthesis gas, containing 17% inerts, enters each of the first-stage ovens, that is, 830 m3 ideal gas ($CO + 2 H_2$), at a conversion of 76% on CO in the first stage 630 m3 ideal gas will thus be converted. The remaing gas per oven will then consist of 200 m3 $CO + 2 H_2$ and 170 m3 inerts + some methane formed in the first stage; in all, therefore, about 400 m3 per oven. The feed to a second-stage oven connected to 3 first-stage ovens will, therefore, be about 1200 m3 total gas containing about 50% inerts.

Production in the second stage is said to be about 20% of the production in the first stage. Three ovens in the first stage will produce : 3000 x 0.83 (total ideal gas) x 100 = 250 kg liquid product per hour. 20% of this quantity, i.e. 50 kg, will be produced in the second stage. Assuming that the gas entering the second stage contains 50% inerts, making from 1200 m3 total gas 600 m3 ideal gas per hour, then the production is about 85 g per m3 ideal gas in the second stage. Actually the production in the second stage amounts to 90 - 100 g of liquid product per m3 ideal gas.

The conclusion which can be drawn from the above is that irrespective of stage, the conversion per converter amounts to about 100 g liquid product per m3 ideal gas.

Further information on the two stages : Poisonous resins deposited on spent catalyst appear to be the same in both stages.

It has been found that the percentage of Co in the catalyst could be decreased, without affecting the production per converter. Originally one oven filled with 3 tons of catalyst contained about 1400 kg Co; later on this was reduced to 850 - 900 kg Co. This refers to atmospheric pressure ovens.

When starting the pressure experiments the latter catalyst was used. This is also the catalyst now being used in the few commercial pressure ovens which are at present in operation under atmospheric pressure. Experimentally, the amount of Co has even been reduced in pressure experiments to an equivalent of 400 kg Co per converter filling.

Every 4 months an oven is taken out of service. It takes about 2 days in all to discharge the oven, refill it again with catalyst and put it into operation.

On an average, 2.5 times during the 4 months' running periods a catalyst is regenerated in situ. Usually the first time this is done is after about 1200 operating hours. Total time for regeneration: 10 - 12 hours. Therefore, total regenerating time per 4 months' running period is 2.5 x 12 = 30 hours. The overall out-of-production time per oven (regenerating, discharging and refilling) is, therefore, 48 + 30, or, say, 80 hours, or per year 240 hours = 10 days. This is about 97% service factor. For the design of the present German plants a service factor of 92 - 93% has been taken.

For design purposes an overall throughput of 820 - 850 m3 ideal gas per converter (1st + 2nd stage) ? 4-5m is taken.

The second-stage ovens do not have to be regenerated, or, at the most, only once during a 4 months' period, because less paraffin is absorbed by the catalyst in this stage, owing to, firstly, less paraffin being produced and, secondly, the scavenging action of the larger amount of inert gases present.

Thus far it has not been necessary to regenerate the catalyst in the pilot plant working under higher pressures. These catalysts have now been 6 months in operation and have, therefore, shown a 100% time efficiency.

7.&9. Number of ovens operating in first and second stage ?

There are 52 atmospheric pressure ovens at Holten. Usually 48 - 50 of these ovens are in operation, about 36 being in the first stage and about 13 - 14 in the second stage.

11. Catalyst volume per oven ?

Atmospheric pressure: total free volume 12.5 m3; catalyst volume: 10 - 11 m3. Pressure ovens: free volume 10 m3; catalyst volume: 10 m3.

This shows that the overall apparent density of the catalyst is a little higher in the pressure ovens than in the atmospheric pressure ovens.

12. Tons of Co per oven ?

850 - 900 kg Co per oven for both atmospheric and higher pressures.

13. Apparent density of catalyst ?

280 - 300 kg/m3.

14. Number of spare ovens ?

At Holten 3 - 4 out of 52 converters.

15. Weight % Co in catalyst ?

In green contact (that is unreduced catalyst) 23% roughly ~~20%~~. This latter catalyst still contains about 7 - 10% water and also a little absorbed CO_2. In final catalyst ~~24 - 26%~~, viz. 850 - 900 kg Co per 3 - 3.1 tons oven charge. -30 - 31% 750 - 950 kg

19. Exact readings from thermocouples in catalyst bed ?

The temperature difference between lower and upper layer of the catalyst in an oven is about 3 - 5°C. Temperature difference, when working with a tube of about 20 mm dia. in the laboratory between the wall and the centre of the catalyst (therefore, about 10 mm distance), is about 15°C.

Practice has shown that the temperature control of the commercial ovens can be done by the steam pressure only. Even in the laboratory no temperatures are taken any longer with a pyrometer tube in the catalyst bed. However, it is realized that the actual temperature on the catalyst surface may be from 100 to a few 100°C higher than the temperature actually measured.

21. Are ovens started singularly or in block ?

All converters in one block are started and shut down together.

22. What is the preferred number of ovens operating in one block from a process point of view and from a plant-size point of view ?

Oven blocks with 2, 4 and 6 ovens are in use at Holten. Dr Alberts does not think that there is any objection from a process point of view to combining 6 ovens in one block. For small plants, however, it will be advisable to reduce this number, as otherwise the service factor will be adversely affected.

23. What is the total amount of fin cooling surface and steam-pipe cooling surface in both low and high pressure ovens ?

Low pressure ovens: 4000 m2 total cooling surface per oven. 10% of this is water-cooled tube surface.

High pressure ovens: 2100 m2 total cooling surface, all being water-cooled surface.

25. Weight of metal per oven exclusive of boiler drum and connections ?

Low pressure ovens : 41 kgt.

High pressure ovens : 48 - 49 kgt, all without insulation.

26. Why are ovens used with a depth of catalyst of 2.5 m ?

Pilot-plant converters have a depth of 1.5 m, commercial-plant pressure converters of 4.5 m. Do not know how far one can go, but too high a catalyst bed would give too much gas on the first layer of catalyst where the gas enters, which could cause trouble through too much heat evolution. Permissible catalyst depth will, therefore, depend on cooling surface and efficiency of cooling means. For this reason Ruhrchemie do not think that the depth of their low pressure converters could be much increased. On one occasion, a fairly large amount of carbon was found to have deposited on the entrance side of the catalyst chamber and warping of the vane tops was noticed. This was not due to too much gas, but was explained at the time by too high an initial activity of the catalyst.

28. Pressure drop per foot of catalyst versus age of catalyst in first- and second-stage ovens ?

Pressure drop does not increase with age of catalyst. Normally the pressure drop is 100 - 200 mm water per oven, both for atmospheric and high pressure ovens, such when using 2 - 3 mm catalyst. It is evident that variation in the size of catalyst will vary the pressure drop.

29. What experiments have been made to prove that oven has been evenly filled ?

Once the pressure drop of all tubes on two cross lines in a pressure converter was measured. The highest variation found was 10%.

31. Have you ever operated high pressure ovens at atmospheric pressure ?

High pressure ovens were operated at atmospheric pressure with same throughput as for the atmospheri pressure ovens. No difference in operation and yield was found. No tests were made in pressure ovens at atmospheric pressure with higher throughputs, but Dr Alberts believes that this will be possible. This question is of importance because the cooling is supposed to be much better in the pressure ovens than in the atmospheric pressure ovens.

32. Why did you choose 15 ft depth of catalyst bed for high pressure ovens instead of using 3 ovens in parallel with 5 ft depth of catalyst bed ?

This was purely a matter of capital costs.

In the pilot plant it was found that with equal <u>space</u> velocity no difference could be determined in composition of the products when varying the <u>linear</u> velocity from 1 to 2 or 1 to 4.

However, different products are obtained when using

a) 1000 m3/h containing 800 m3 CO + 2 H_2

versus

b) 2000 m3/h containing 800 m3 CO + 2 H_2.

Lighter products are obtained when the gas contains more inerts.

In general it can be said that at the same temperature but with higher throughputs the products obtained are lighter.

With same throughput but varying temperatures lighter products are obtained at higher temperatures.

33. Have you ever emptied an oven layer by layer and examined the catalyst from each layer in the laboratory to determine whether the decline in activity of the catalyst is the same at top and bottom ?

Activity decreases from top to bottom. A comparatively fresh catalyst will show much higher activity in the bottom layers than in the top layers, the latter ones being poisoned, of course, first. After some time of running, however, the bottom layers will get poisoned also, so that the activity of the catalyst at top and bottom will then be about equal.

34. What is your present recommendation for ideal construction of low pressure ovens ?

Converters with catalyst in tubes.

When not considering yield per m3 gas but only yield per g Co, one can use wider tubes when increasing the linear velocity. Dr Alberts believes that when circulating gas, such as, for instance, tail gas or CH_4, to remove the reaction heat it will be necessary to recirculate about 5 or 6 times the volume of fresh feed.

When using the same gas quantity the conversion with a 2 - 3 mm catalyst will be about 70% CO in the first stage, whilst when using a 0.5 - 1.0 mm catalyst the conversion will be about 90% CO.

One can reach also in the latter case a conversion of 70 - 75% CO by increasing the throughput by 35%. This is due to better heat dissipation.

For commercial ovens Dr Alberts would recommend the following:

Tubes of 10 mm dia., thickness of wall: 0.75 mm or as thin as possible. Material of tubes, if possible, Al; length of tubes: 4 - 5 m. Catalyst: hard as stone; if possible, less than 1 mm.

However, it is pointed out that a small quantity of dust is worst for a 0.5 - 1 mm than for a 2 - 3 mm catalyst. The shorter the tubes, the smaller the pressure drop and the more difficult it is to obtain an even gas distribution over the tubes. However, apart from gas distribution 500 tubes of 1 m are to be preferred to 100 tubes of 5 m.

35. Have you ever visualized connecting a number of cooling tubes to different headers in order to control temperature in direction of flow ?

Trials have been made in connecting a number of cooling tubes to different headers, in order to control temperature in direction of flow. No great difference was found in the results. A real advantage could not be ascertained; probably the products are somewhat more saturated.

36. Have you ever made experiments with upflow through catalyst bed tending to show that you can operate with 1/2 or 1/4 of the normal catalyst bed thickness ?

Experiments with upflow through catalyst bed have been made. It was stated that in this case no great difficulties had been encountered with clogging up of the bed. However, after a fortnight the experiments with a low pressure oven had to be terminated on account of leakage. A h.p. pilot tube clogged up after 2 to 3 months. Probably the upflow will produce some more paraffins, but with slight difference as compared with downflow. Dr Alberts does not think much of the cooling effect of the reflux.

37. Analysis of synthesis gas entering first stage, leaving first stage and leaving the second stage ?

The analyses of the gas entering and leaving first stage and leaving second stage are as follows:

	entering first stage	leaving first stage	leaving second stage
CO	28	17	6
H_2	55	32.5	10
CH_4	0.4	8	17.8
CO_2	13.5	35.5	55
N_2	3.1	6.5	10
Olefines	-	0.5	1.2

Conversion after 1st stage : 72 - 75% CO
Total conversion after 2nd stage : 92 - 95% CO

38. What are the properties of the gasol fraction after first stage and after second stage ?

The properties of the gasol fractions after first and second stage do not change.

Some time ago activated charcoal was used after the first stage; this was discontinued 7 months ago, as there was no difference to be found.

39. Have you any results when operating with a synthesis gas as produced directly in the water gas generator ?

A synthesis gas, consisting of 1 CO - 1.5 H_2 has been used.

It appeared that with l.p. operation, with Co-Th as a catalyst, the catalyst life was shorter (about 4 weeks) and that the liquid products were lighter.

The olefine content in the light gasoline was increased from 40 to 60% with an octane number of 68.

It is expected that more suitable catalysts may be found for the purpose of operating with a synthesis gas as produced directly in a watergas generator.

An experiment with Co-Mg catalyst under pressure is in progress. Yield is the same as with synthesis gas 1 : 2. During 2 months catalyst activity did not increase. There is some difference in olefine content of products between running at 5 atm. and at 10 atm.

It is interesting to note that under 7 atm. pressure working with watergas, about the same products (as far as boiling range and olefine content are concerned) are obtained as at normal pressure when working with gas containing $CO:H_2$ in ratio 1 : 2.

As Ruhrchemie are less interested in paraffin production, they, therefore, intend running their full-scale plant under pressure with watergas if the experiment should prove successful. In the second stage, they will then add some H_2, in order to obtain a better CO conversion.

The pressure of units in the second stage, also in the case of watergas as raw material, leads to a lighter product.

In case it should prove advantageous to run the second at a higher pressure, this will be possible, because the h.p. compressors can deliver the gas up to 15 atm. on account of the tail gas of the first ~~stage having a higher specific gravity than the~~ synthesis gas.

31. Reactions involved in organic sulphur removal ?

The reactions involved in organic sulphur removal are as follows:

After primary purifying, the gas contains 12 - 20 g/100 m3 sulphur in the form of about 60% carbon disulphide (CS_2) and about 40% carbon-oxy-sulphide (COS).

These figures, of course, depend on quality of coke and the way the generators are run. These compounds are converted into H_2S with the aid of H_2 present, and are taken up by the sodium carbonate; the reaction is promoted by the iron oxide.

A small percentage of oxygen (0.1 - 0.2%) is necessary to oxidize the sulphides into sulphates; air may be used for this purpose.

In the beginning no oxygen was added, but in that case the H_2S "breaks through" more easily, and the saturation could not be carried on higher than 7%, whereas now with the addition of oxygen, the saturation may go on up to 10%.

It is important that the purifying mass should be very porous, in which respect lux mass is quite satisfactory. It was stated that any kind of porous iron hydroxide is suitable, such as, for instance, "Raseneisenerz". Al-content is immaterial. This purifying mass consists of 66% FeO and 34% Na_2CO_3. The temperature when purifying is about 200 - 300°.

Cyclic-bound sulphur will not be removed, but mercaptans are.

Cyclic sulphur compound is contained in gases when produced in generators operating at relatively low temperature, but will be cracked at 1100 - 1200°C; consequently, the Holten synthesis gas does not contain such compounds.

The price of lux mass was stated to be RM 14.50 per ton, containing 50% water; calcinated soda RM 100.- per ton and the price of finished purifying mass was said to be RM 90.- to RM 100.- per ton.

Questions 45 and 46:

45. Why is the addition or oxygen necessary ?
46. If the answer to 45 is to produce sulphates why do you have to make sulphates ?

have also been answered by the above.

44. Is a reducing atmosphere necessary for sulphur removing ?

Investigations will be carried out to answer the question whether a reducing atmosphere is necessary for sulphur removing.

47. What is the maximum space velocity used successfully in sulphur removal towers ?

As regards the question of the maximum tolerable space velocity in organic sulphur-removing towers, the following answer is given:

Two types of towers are in use:

	set of two towers	
a) screen towers (trays)	cap. 20,000 m3 gas/h	cont. 50-60 m3 mass each tower
b) cylindrical towers	cap. 25,000 - 28,000 m3/h (probably more)	cont. 90-100 m3 mass each tower.

The towers are used in sets of 2, placed one after the other, for the sake of greatest possible safety and economy.

When the first tower is saturated up to 10-11%, the set is taken out of operation and, after re-filling, the second tower is placed first.

The specific gravity (app.dens.) of the mass is 0.8.

A high porosity is necessary, therefore, no balls or pellets can be used.

48. You have two designs of towers; which do you prefer ?

For handling the heavy bells of the H_2S removal, hoisting equipment is necessary and this crane is also available for the second purifying step, thus making the use of screen (tray) towers, which are slightly less expensive than the cylindrical towers, possible. One tray at Holten has a weight of about 30 tons.

49. Do you have both types of towers in operation at Holten ?

At Holten 5 screened towers and 5 of the other type are available, i.e. in all: 5 sets of 2 towers. In operation there is no difference.

50. Do you recommend a heat-exchanger or cooler between towers ?

A heat-exchanger between the towers is unnecessary, as about the same temperature in both towers is satisfactory.

51. What is the analytical procedure for organic sulphur determination ?

The sulphur content of the purified gases is determined by combustion. The gas is passed through an analysis apparatus at the rate of 100 L/h , yielding after 4 hours sufficient sulphur to be determined as Ba sulph. This procedure has been described in "Brennstoffchemie". Heating the gas at 1000° in a quartz tube filled with quartz chips with the hydrogen present and determining the H_2S as CdS, is a shorter method.

52. How many grams of sulphur are deposited on catalyst when towers are changed from second stage to first stage and towers are removed ?

Regarding the shifting of towers, the following is stated:

The life of one tower is 83 days.

If one tower is taken out for renewing of the mass, also the second tower goes out of operation.

A cooling of the mass with circulating synthesis gas or tail gas is applied; otherwise the hot mass would glow when coming into contact with air, which would de detrimental to the transport belts and further equipment.

Part of the removed mass, which apparently has not yet been completely saturated, is separated, granulated and used again in the H_2S removal. The cooling, discharging and refilling of a tower takes 24 hours.

Dr Alberts mentioned the possibility that in future or in other installations both purifying steps may be replaced by other systems, e.g. a Linde-Fränkl process, in which the gas is purified from CO_2, H_2S, organic sulphur and gum by regenerative cooling down to -180° /-190°. In this process a scavenging gas is applied to remove the condensed impurities, for which Linde require nitrogen, involving high costs. Dr Alberts thought it possible to use air for this purpose, but Linde refuse to build such a plant.

33. What is the total utility consumption and the net utility consumption, exclusive of the watergas generators and synthesis product-treating units (steam, electrical power, water and fuel gas) ?

The utility consumptions are given as follows:

1) gas consumption for organic sulphur removal 4% of calor. value of the gas to be treated; the flow chart ZM 106/19 estimates this figure to be 116 cal. per m3 synthesis gas.

2) for distilling fuel consumption 2%.

3) when working under pressure, the heating of the fat oil from the oil absorption plant will require 1 - 1½% of the calor. value of the products condensed.

4) steam consumption for the final purifying: nil.

5) steam consumption of the synthesis: merely for starting up the processes (heating of the ovens), this quantity is about 1 ton/h steam of 20 atm. for a plant of 100 converters.

6) for the condensation of the heavy products in a plant working at atmospheric pressure, no steam is necessary. The activated charcoal plant requires 2 - 2.5 kg low-pressure steam of 2½ atm./kg gasoline produced.

If C_3 and C_4 are produced in large quantities, the steam consumption is to be set at 4½ kg/kg C_3 and C_4.

An average figure for Holten is about 3 kg/kg light benzine, incl. C_3 and C_4.

The steam produced in the synthesis at Holten amounts to 5 kg per kg liquid products.

7) When working under pressure no steam is used for condensing heavy benzine, which needs only indirect water cooling; the light parts are absorbed in oil; for removing the vapours from the fat oil, steam cannot be used, it having an insufficient temperature; the fuel consumption is about 1½% of the cal. value of the oil produced.

8) The electrical energy consumption, assuming that no steam is used, may be stated as follows:

For H_2S removal, a small quantity for circulating air during the emptying of the vessels.

For organic S-removal about 20 kW for each set of purifiers with a capacity of 20,000 m3/h . This figure includes the blowers for air and circulating flue gas.

The electrical consumption for the synthesis is about 0.75 kW per oven for feed pumps, hydrogen blowers (intermittent), crane, etc.

9) For circulating cooling water pumps, 30 kW per ton total liquid products are required, this figure including also products pumps for synthesis at atmospheric pressure.

10) If the activated charcoal plant has to recover a large percentage of gasol (80-90%), a circulating blower is used with a consumption of 25 - 30 kW/ton total liquid products.

11) For the compression of propane-butane produced as gas (containing about 60% C_3C_4) from the activated charcoal plant, the electrical consumption is 150 kWh per ton C_3C_4.

12) When working at atmospheric pressure, the gas

transport blowers working at a pressure of 3000 mm have a power consumption of 15 kW for 1000 m3 gas.

When working at 10 atm., the turbo compressors consume 128 kWh/1000 m3, thus for 80,000 m3/hour, 10,000 kW ! /

13) The cooling water is circulated; for losses and evaporation a quantity of 50 m3 per ton of liquid primary products has to be supplied, including boiler feed water. This figure relates to the synthesis alone; for the complete process, incl. cracking and distillation, this figure would be about 70 m3./ for gasoline 140 l.

The circulation at Holten amounts to about 1500 ~~500~~ m3/hour.

56. Weight of steel required for each step ?

The weights of steel required for each step are given as follows:

H_2S removal		1000	tons	per	40,000 m3 gas/h	
organic S removal		475	"	"	"	"
synthesis:	one l.p. converter	45	"	40		
	one h.p. converter	43	"	49		
pipe connections, fittings, boiler drum, etc. about		8	"	"	converter	
synthesis bldg, supports & roof, incl. crane, excl. walls		3-4	"	"	"	
Condensing plant for l.p.		250	"	"	40,000 m3 gas/h	

? Activated charcoal plant, incl. absorbers, steel structure, blower pipe connections, fittings, etc.	800	tons	per	40,000 m3	gas/h
Condensing plant for h.p. incl. coolers	130-150	"	"	"	"
Oil absorption plant with heaters, etc.	about 300	"	"	"	"

57. Capital cost of each step ?

The capital cost for a plant of 40,000 m3 synthesis gas/h is given as follows:

H_2S removal (all erected, incl. foundations)	RM	500,000
Organic S removal (all erected, incl. foundations)	"	350,000
Synthesis per oven, incl. pipe connections, instruments, foundations, building and erection costs, excl. catalyst :		
for low pressure : RM 63,000/	"	65,000
" high " :	"	72,000
Condensing plant, two stages for low pressure :	"	300,000
? Activated charcoal plant, excl. charcoal : (charcoal 100 tons at RM 2000/ton)	"	800,000
Condensing plant, high pressure	"	250,000
Oil absorption plant (incl. pipe stills, etc.)	"	600,000

Blowers, 40,000 m3/h , 3000 mm H_2O each, incl. motor	RM 30,000
Ditto, 80,000 m3/h , incl. motor	" 37,000
H.p. compressor unit for 10,000 m3/h incl. bldg, foundations, pipe connections and erection	" 220,000
Complete compressor plant at Holten with 4 units :	RM 1,600,000

58. Labour cost for each step ?

The labour costs are stated to be as follows:

For purifiers and blowers up to 80,000 m3/h	3 men per shift
For purifiers and blowers 160,000 m3/h	4 " " "
For synthesis plant of 100 ovens	6 " " "
Moreover, for small repairs, cleaning, changing of catalyst (working mostly in daytime only)	10-15 " " "
Condensation (for pumps)	1 man " "
Activated charcoal plant and gasol production	2 men " "
For control laboratory	5 chemists 6 helpers } per day

Repair shop	15-20 men per shift
working two shifts, making in all	30-40 "
Repairs in the plant are executed by these men; part of these are also employed for the ammonia plant.	

59. Cost of maintenance and repairs for each step ?

The costs of maintenance and repairs are 1-1½% of the total capital cost. This figure includes labour and material, but only for the synthesis plant without watergas production.

60. Cost of miscellaneous supplies ?

The costs of miscellaneous supplies are difficult to estimate; for the plant at Holten a rough figure of RM 100,000/year was given.

61. We should like a flow diagram showing type, material and cost for each piece of apparatus.

Regarding the materials used for the various apparatuses, etc., it is answered that only normal iron has been used in the plant, with the exception of the valves, for which a chrome-nickel alloy (2% and 1% respectively) is applied. Moreover, for the h.p. condensers special tubes are used, containing chrome and nickel (probably 5-6% chrome and 3% nickel); the tubes of the heaters in the organic sulphur removal contain 4-6% Cr.

CHAPTER VII.

CONTROL & RESEARCH LABORATORY.

PILOT PLANT CONVERTERS AND INVESTIGATIONS.

A. CONTROL & RESEARCH LABORATORY.

In the Laboratory the various starting materials for manufacturing the catalyst are very carefully analyzed and further a minute control is performed on the preparation of the catalyst in the catalyst plant, although this plant itself analyses the liquids handled during the manufacturing processes. Although in this way an excess of impurities, etc. is easily detected, and can be corrected forthwith, it occurred that the catalyst produced proved to be unsatisfactory. Therefore, the laboratory has the task of taking samples of the purified solution and precipitating the cobalt and the oxides on Kieselguhr, whereafter the catalyst manufactured in this way is tested in specially built laboratory converters.

These consist of glass tubes of about 5/8" dia., placed in sets of 3-8, mostly 6-8, in an aluminium electrically-heated oven, with a special arrangement to keep the temperature constant. Synthesis gas is led over the catalyst and the condensed liquids are measured and analysed periodically. In the laboratory more than 200 samples of catalyst are tried out simultaneously, part of which originate from catalyst plant solutions, part being tried out for research purposes.

The first-mentioned tests are run for some weeks only; of the latter some samples were running for more than a year.

It was stated that in this way the manufactuning process of the catalyst plant can be controlled without unexpected failures.

The price of one oven block together with temperature control is about RM 500.-

Separate from this, similar apparatuses are used for investigating lifetime and yield of different types of catalyst under pressure.

As an example of the investigations in progress it was mentioned that catalysts are being tested having only half the amount of CO as compared with the normal catalysts. Results look promising, but no final conclusions can as yet be drawn as to their lifetime. Co

B. PILOT PLANT CONVERTERS AND INVESTIGATIONS.

Five pilot plant converters are housed in a building of about 12 x 16 m. These converters are of different size and construction and have different capacities. Each of these converters will be discussed briefly.

1. Same construction as the high pressure commercial converters, but 1/10th of their size.

Tubes consist of an inside and outside tube with the catalyst in between; inside diameter of outside tube 54 mm, outside diameter of inner tube 34 mm; (see Annex A, fig. 13 B).

converter diameter	1.30 m	
catalyst volume	1,000 L	
gas rate	100 m3/h	on day when visiting this plant.
pressure	3 atm.	

2. Converter diameter	900 mm	
height	2½ m	
catalyst volume	400 L	
gas rate	40 m3/h	on day when visiting this plant.
pressure	7 atm.	

Tubes of 34 mm having a thin metal sheet pressed into them and spot welded on three sides (see figure 13 A, Annex A). Catalyst filling entire space inside of tube.

3. Converter diameter	about 900 mm	
height	2½ m	
catalyst volume	300 L	
gas rate	30 m3/h	on day when visiting this plant
pressure	5 atm.	

Tubes 10 mm diameter.

This small converter already contained 1550 tubes. It was calculated that a commercial-size converter of this type would contain 35 km tube length of this diameter. It would take the entire Mannesmann outfit 4 years to manufacture enough converters of this type for a plant like the one of Ruhrchemie.

4. Converter diameter	about 1200 mm	
height	2.4 m	
catalyst volume	805 L	
gas rate	80 m3/h	on day when visiting this plant,
pressure	5 atm.	

Tubes: same construction as those of the commercial high pressure converters and the pilot plant converter mentioned under 1.; however, the diameters in this case were 44 mm inner diameter of outside tube, 24 mm outside diameter of inner tube.

5. Converter diameter	900 mm
height	1.30 m
catalyst volume	300 L

This converter was not in operation when visiting the plant. It has a peculiar design in so far that it consists of two metal sheets welded together on the 4 sides, but leaving a small volume in between and then wound like a spring. (See fig. 13 E, Annex A).

Cooling is done by water circulating inside the two metal sheets welded together, the catalyst filling up the entire space of the spring-like wound metal sheets and the largest distance between the two sheets being 10 mm. This is, therefore, the same kind of construction as used for "Imperial" coolers.

The cooling in all these experimental converters is done by water and the temperatures are controlled in the usual way by steam pressure, the boilers being designed as vertical tubes with a diameter of 8" and a working pressure up to 50 atm.

We were told that the best cooling was obtained in those converters where catalyst had water on both sides (inside and outside as in the converters mentioned under 1, 4 and 5).

Most experiments had been made at 5, 7 and 10 atm. The higher the pressure the heavier the product produced and the less gasol and CH_4 obtained.

At higher gas rates lighter products are obtained.

When doubling the gas rate the "Leistung" is increased about 1.5 times, when leaving the temperature the same, or 1.8 times, when increasing the temperature to maintain the same CO conversion. In the latter case relatively more CO is lost as CH_4. Rough figures given in this respect:

1.	100 m3 gas/hour	185°C.	75% CO conversion
2.	200 " " "	185°C.	say 58% " "
3.	200 " " "	say 200°C.	75% " "

In case 3 more CH_4 and in case 2 about the same amount of CH_4 is produced as compared with case 1.

An experiment was made with one of the pilot plant converters to see whether the reaction heat could be removed by adding tail gas to the fresh feed and circulating this tail gas back into the reactor via a cooler. It was found that about 5 times the amount of fresh feed as tail gas was sufficient to prevent any evaporation of the water left inside the cooling tubes in the reactor.