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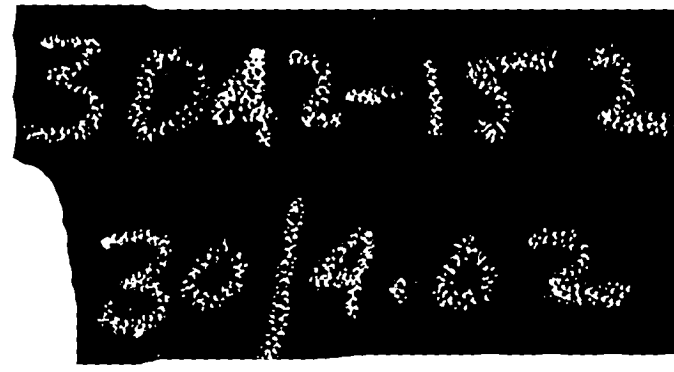

Hydrocarbon Synthesis
from
Mixtures of Carbon Monoxide and Hydrogen

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Hydrocarbon synthesis from mixtures of carbon monoxide and hydrogen.

REPORT

on

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

2. Discussions between U.S.A.C. partners in Ludwigshafen.

25th October till 1st December 1938.

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INTRODUCTION

After conclusion of the hydrocarbon synthesis agreements delegates of the various partners in the U.S.A.C. (viz.: I.G., Standard of New Jersey, Kellogg and Shell) came together at Ludwigshafen in the end of October 1938, in order to study the Fischer process as developed and applied by Ruhrchemie and further to exchange technical information available amongst parties.

A report on the synthesis as carried out in Ruhrchemie's plant at Holten, made up according to the contract, was distributed.

In the following days verbal explanation was given by Ruhrchemie.

Hereafter the Ruhrbenzin plant was visited on various occasions by delegates of all partners, while also further extensive explanations were given.

Furthermore another meeting was held at Ludwigshafen by the delegates of the U.S.A.C. partners only (thus without Ruhrchemie), at which firstly the production of synthesis gas was discussed, secondly I.G. and Kellogg communicated about their respective research work done on the synthesis of hydrocarbons from mixtures of carbon monoxide and hydrogen.

It was agreed that a summarizing report of all the information collected on the above-mentioned subjects should be drawn up by Kellogg and submitted to the U.S.A.C.

The following report is a synopsis of the notes of the Shell and I.H.P. delegates.

- - - - -

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 by distillation and cracking.

Note: For full details about the properties of the primary products obtained both at normal and at elevated pressure see Annex F (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.

Discussions in Ludwigshafen.

During these discussions the research work done by the U.S.A.C. partners was discussed.

1. Re production of synthesis gas from gaseous hydrocarbons.

Kellogg have investigated the partial combustion of methane with oxygen and came to the conclusion that this method is too expensive.

They believe that a regenerative method using the methane-steam-carbondioxide reaction will be promising. No experiments, however, have as yet been carried out.

As the methane-reforming converters in Shell Point (U.S.A.) might be applied for such a process, Mr Langen van der Valk (Shell) gave a survey of the operating conditions and results obtained in this plant.

I.G. have carried out semi-technical experiments on synthesis gas production from gaseous hydrocarbons by partial combustion of methane with oxygen and by catalytic and non-catalytic conversion of methane with steam and carbondioxide.

2. Re synthesis.

I.G. are carrying out investigations in various laboratories, which up to now have worked independently of each other.

In Oppau laboratory research mainly directed for finding catalysts suitable for paraffin wax production is going on.

In Leuna investigations are being carried out in 16 semi-technical units both for pressure and atmospheric work; in addition a large number of catalysts is continuously being tested in the laboratory. Leuna could confirm results obtained by Fischer; Fischer type catalysts are being used.

In Oppau and Ludwigshafen respectively two other processes are being investigated on a semi-technical scale, both using iron catalysts and working under pressure. These processes are different from the original Fischer process.

New methods are applied for removing the heat of reaction. The catalysts used are of a different type (much cheaper). The products contain a high percentage of olefines and a high "Leistung" (amount of liquid product obtained per unit of time per unit of catalyst volume) is obtained.

As synthesis gas, mixtures of CO and H_2 in proportion 40 : 60 to 55 : 45 are being used.

In one of these processes (plant at Oppau) the heat of reaction is carried away by recycling the heavier part of the liquid hydrocarbons produced. This process works at present at 100 atm., but experiments are also being carried out at 20 atm.

The primary product contains 42 % up to 200°C. The O.N. of this fraction is 68.

According to the second method (plant in Ludwigshafen) the heat of reaction is taken away by applying a large recycle ratio of tail gas working with a very short time of contact and a low percentage conversion per pass.

This process operates at 20 atm.

The primary product contains about 80 % olefines. 45 % of the primary product consists of gasoline (-200°C), having an O.N. after refining of 77 m.m. and a high blending value.

Kellogg feel that in the U.S.A. synthesis gas may be produced at very low costs from natural gas, large quantities of which are wasted at present. Investigations, therefore, were mainly directed to arriving at a larger production per unit volume of catalyst in order to reduce the capital costs of the synthesis plant. A large number of laboratory experiments were carried out.