HYDROCARBON SYNTHESIS

FROM

CARBON MONOXIDE AND HYDROGEN

February 27, 1939

THE M. W. KELLOGG COMPANY
IABORATORY II

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* A more detailed index immediately precedes each major subject discussion.

FOREWORD

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This report attempts to present the information made available to USAC in a series of meetings and plant visits in the period from the latter part of October to the first of December, 1938.

The original plan was that Kellogg should write the report using the composite notes of all companies represented at the meetings. Due to delay in receipt of the notes from the member companies, this report was written on the basis of notes by the Kellogg representatives, although the several numerical quantities have been compared with those given by the other companies.

INTRODUCTION

INTRODUCTION

The experiences of the member companies of USAC and of Ruhrchemie upon the production of liquid hydrocarbons from raw materials, by way of the reduction of carbon monoxide with hydrogen, have been given in a series of meetings held in Germany in the late autumn of 1938. The information made available has been organized in this report as to subject matter and as to origin. The subject matter was arbitrarily divided into three sections:

I. Manufacture of Synthesis Gas

II. Manufacture of Synthesis Catalysts

III. The Operation of the Synthesis Reaction

Under each of these headings, the material from each company has been presented separately.

The quantities and dimensions have been given first in the units in common use in the United States and immediately following, in parentheses, in metric units. It should perhaps be mentioned that all "tons" in the parentheses refer to metric tons, i.e., 2200 pounds. A tabulation of the conversion factors employed will be found on the first page in the appendix.

A fourth section of the report is made up of items of information that did not logically fall under the main divisions mentioned on the preceding page.

SUMMARY

The material covered in this report is not of such nature that it may be adequately summarized. Therefore, only the essential information pertaining to each section of the report will be set down here. Any comparison of the various processes would best be made with consideration of the several details of each operation.

SUMMARY

Synthesis Gas Manufacture

Ruhrchemie

At Holten, synthesis gas containing hydrogen and carbon monoxide in the ratio of two-to-one was made by the conversion of a part of the carbon monoxide in water gas, which in turn was made from coke in water-gas generators. The synthesis gas was purified by passage over an iron contact, until the total sulfur content was less than 0.06 grams per thousand cubic feet (0.2 grams per hundred cubic meters). The Holten plant (eleven generators) had a daily capacity of about 75,000,000 cubic feet (2,000,000 cubic meters) of synthesis gas.

Synthesis Gas Manufacture

I.G. Farbenindustrie

Synthesis gas had been made continuously from methane, water and carbon dioxide in tubes externally heated to 1400°F. (750°C.) at the rate of 1000 volumes of synthesis gas per hour per volume of catalyst. In an intermittent regenerative process, only 20 volumes of synthesis gas per hour per volume of catalyst could be produced.

In a Cowper regenerative set, synthesis gas could be produced at the rate of 70-100 volumes of gas per hour per volume of packed furnace, using as raw material a gas containing 40% hydrogen, 40% hydrocarbons.

Synthesis Gas Manufacture

Kellogg

Synthesis gas with a ratio of hydrogen to carbon monoxide of two-to-one was made from methane and oxygen in externally heated tubes on a laboratory scale at the rate of 900 volumes of gas per hour per volume of catalyst. Synthesis gas with a ratio of hydrogen to carbon monoxide of one-to-one was made from methane and carbon dioxide, in the above mentioned equipment, at the rate of 1000 volumes of gas per hour per volume of catalyst. From a gas containing 50% hydrogen, 30% methane, synthesis gas with a two-to-one ratio of hydrogen to carbon monoxide could be produced at the rate of 700 volumes of gas per hour per volume of catalyst. The catalyst was nickel-ceria or nickel-thoria supported on Alfrax.

Commercial estimates indicated that the most economical method of synthesis gas production from methane was the reaction of methane with carbon dioxide and water in a regenerative process, where synthesis gas would be produced at the rate of 500 volumes of gas per hour per volume of catalyst at temperatures of 1800-2200°F. (980-1200°C.).

Hydrogen Manufacture

Shell

A natural gas containing 75% methane and 23% ethane was cracked in a regenerative furnace to the extent that all the ethane and about 50% of the methane disappeared. Hydrogen-rich gas was produced at the rate of seven volumes of gas per hour per volume of furnace.

Synthesis Catalyst

Ruhrchemie

The synthesis catalyst used at Holten was prepared by precipitation of cobalt, magnesium and thorium as carbonates, from a nitrate solution, upon kieselguhr, using sodium carbonate as precipitant. The precipitate was dried, formed into particles from 1 to 3 millimeters and reduced with hydrogen. The composition of the reduced catalyst was 32% cobalt, 2.5% magnesia, 1.5% thoria and 64% kieselguhr (Co:0.08 MgO:0.05 ThO_2:2.0 SiO_2).

Synthesis Catalyst

I.G. Farben-industrie

The iron catalysts were prepared by the fusion of iron and small amounts of activators in an oxygen flame, sizing the fused mass and reduction of the particles with hydrogen at high temperatures. The composition of the reduced catalyst was not given, but it contained upwards of 90% iron.

The precipitated cobalt catalysts had about the same composition and were prepared in a manner similar to that described for the Ruhrchemie catalyst.

Synthesis Catalyst

Kellogg

Various cobalt and nickel base catalysts have been prepared and tested, but most of the work was done upon the cobalt-thoria-kieselguhr catalyst (Co:0.17 ThO_2:2.0 SiO_2). The latter was prepared in a manner similar to that used by Ruhrchemie.

Synthesis Reaction

Ruhrchemie

About 800 barrels (90 tons) of oil were being produced daily at Holten from a total of 52 reaction chambers operating at atmospheric pressure. The yield of oil was about 120 grams per cubic meter of synthesis gas, which corresponded to a production of 0.35 gallons of oil per day per pound of cobalt (2.1 tons of oil per day per ton of cobalt) or 1.9 gallons of oil per day per cubic foot of catalyst (180 kilograms of oil per cubic meter of catalyst). The catalyst had a life of about four months at atmospheric pressure and would produce about 43 gallons of oil per pound of cobalt (255 tons of oil per ton of cobalt) per lifetime. The overall production corresponded to 2.65 barrels of oil per year per pound of cobalt in the plant (665 tons of oil per year per ton of cobalt).

The installation of 72 additional synthesis reaction chambers for operation at seven atmospheres pressure was well under way. Upon completion, the oil production at Holten was expected to be in excess of 2000 barrels daily. In the pressure operation, the oil yield was about 145 grams per cubic meter of synthesis gas, which corresponded to a production of 0.44 gallons of oil per day per pound of cobalt (2.6 tons of oil per day per ton of cobalt) or 2.3 gallons of oil per day per cubic foot of catalyst

(225 kilograms of oil per cubic meter of catalyst). Under pressure, the catalyst had a life of about six months and would produce 77 gallons of oil per pound of cobalt (484 tons of oil per ton of cobalt) per lifetime. The above production would correspond to 3.2 barrels of oil per year per pound of cobalt (800 tons of oil per year per ton of cobalt).

Synthesis Reaction

I.G. Farbenindustrie

The iron catalyst, at a pressure of 1500 pounds per square inch (100 atmospheres) over which oil was circulated to remove the heat of reaction, was used in a single stage with a conversion of about 50% of the synthesis gas. The oil yield (including propylene and all heavier hydrocarbons) was 67 grams per cubic meter of synthesis gas, which corresponded to a production of 0.3 gallons of oil per day per pound of catalyst (1.74 tons of oil per day per ton of catalyst) or 37.5 gallons of oil per day per cubic foot of catalyst (3.5 tons of oil per day per cubic meter of catalyst). The catalyst life was not known except that it was in excess of 1500 hours. If 1500 hours be assumed as the lifetime, about 19 gallons of oil would be produced per pound of catalyst per lifetime (109 tons of oil per ton of catalyst per lifetime).

The iron catalyst, at a pressure of 300 pounds per square inch (20 atmospheres) over which gas was circulated to remove the heat of reaction, converted about 75% of the synthesis gas. The oil yield (including propylene and all heavier hydrocarbons) was about 96 grams per cubic meter of synthesis gas, which corresponded to a production of 0.04 gallons per day per pound of catalyst (0.25 tons of oil per day per ton of catalyst) or 6.9 gallons of oil per day per cubic foot of catalyst (0.64 tons of oil per day per cubic meter of catalyst). The catalyst life was about 2-1/2 months and the above rates would correspond to an oil production of about three gallons of oil per pound of catalyst per lifetime (23 tons of oil per ton of catalyst per lifetime).

The yields of oil from the precipitated cobalt catalysts were said to be in agreement with those reported by Ruhrchemie.

Synthesis Reaction

Kellogg

The yield of oil was about 88 grams per cubic meter of synthesis gas, which corresponded to a production of 1.44 gallons of oil per day per pound of cobalt (8.4 tons of oil per day per ton of cobalt) or 7.5 gallons of oil per day per cubic foot of catalyst (0.7 tons of oil per cubic meter of catalyst volume). The life of the catalyst

was not known, but if it be assumed to be three months, the oil production per lifetime of the catalyst would be about 132 gallons per pound of cobalt (770 tons of oil per ton of cobalt).

Synthesis Reaction Summary

The preceding data upon the synthesis reaction has been summarized in the following tabulation. The data from Ruhrchemie have been changed to include propane and butane, in order to get the data on a basis comparable with that from the other companies:

Process	Yield g./m³	Production gal./day/lb. Co(Fe)	gal/day /cu.ft.cat.	gal/lb. Co(Fe) /life
Ruhrchemie - 1 atm.press.	135	0.39	2.1	48
Ruhrchemie - 7 atm.press.	155	0.47	2.5	87
I.G. Oil circulation	67	0.30	37.5	19*
I.G. Gas circulation	96	0.04	6.9	3*
Kellogg	88	1.44	7.5	132*

* Estimated life.