

Introduction

We have published some time ago a paper under the title "Approximation to the Theoretically Possible Yields of the Fischer-Pichler Middle Pressure Synthesis" 1/. The experiments were conducted with cobalt-thorium catalysts. The yields in solid and liquid hydrocarbons (without counting about 13 g gasol) amounted under normal conditions to 150 g with a maximum of about 170 g/ncbm of the ideal gas. Under the most favorable conditions solid paraffines formed over 1/2 of the product.

Franz Fischer and his collaborators have tried ever since the beginning of their work on the synthesis of hydrocarbons from carbon monoxide and hydrogen to substitute cheaper catalysts for cobalt and thorium. Attempts to use iron catalysts were made repeatedly. In 1923 Franz Fischer and Tropsch 2/ have obtained a mixture of the most varied oxygenated compounds by conducting water gas over alkalized iron at pressures at about 100 atm and at 350 - 450°C, and have named the product obtained synthol. The Badische Anilin- and Sodafabrik 3/ have worked since 1913 at similar pressures and temperatures and have succeeded in 1925 to synthesize methanol. Franz Fischer and Zerbe 4/ have shown, also in 1923 that when the pressure was reduced, the alkalized iron filings acted as a catalyst upon carbon dioxide and hydrogen passing through an intermediate formation of carbon monoxide and hydrogen with ever increasing amounts of hydrocarbons. Their work was done in a circulation apparatus at 410°C and at pressures down from 100 - 105 atm. At high pressures only water soluble products were obtained, but at pressures of 7 atm, down to which the experiments were continued, some oil has been obtained, which, as has been shown in communications at that time, contained some 40 percent of products insoluble in concentrated sulfuric acid, and which were similar to petroleum in character.

Franz Fischer and Tropsch 5/ stated in 1926 in connection with their publication on the synthesis of petroleum, that at temperatures of 300°C and above and with iron catalyst, carbon monoxide and hydrogen can interact at atmospheric pressure with the formation of hydrocarbons. Starting with this fact, they have recurrently tried in the following years to increase the activity of the iron catalyst by changing the method of its preparation and by making certain additions to

it, and lower in this way the reaction temperature as well as raise the yield in liquid hydrocarbons. In 1928 ^{6/} at atmospheric pressure, 30 - 40 g of gasoline and oil were obtained/lcbm of water gas. The temperatures could be lowered to 240 - 250°C. The life of the catalysts amounted to a few days.

In 1927 Franz Fischer and Tropsch ^{7/} have also tried to convert water gas at 10 - 15 atm pressure and at 250 - 280°C. The iron-copper catalyst obtained by the ignition of the nitrates were put in operation directly with water gas. The reaction products obtained contained water-soluble and oily substance in proportion of 3 : 2 to 1 : 1. The authors have then stated that the results were poorer than when operating at atmospheric pressure. In the year 1934 Franz Fischer ^{8/} has however stated in a summarizing article on gasoline synthesis, that 1 cbm mixed gas at atmospheric pressure produced a maximum yield of 30 - 35 g with iron catalyst (which corresponds to about 40 - 45 g/cbm of carbon monoxide - water mixture), and they stated further that this initial yield dropped by about 20 percent in 8 days.

In 1934 - 1936 Franz Fischer and Meyer ^{9/} have again tried to increase the liquid hydrocarbon yield by improving the activity of the iron catalyst. They used an iron-copper precipitated catalyst at atmospheric pressure and succeeded in obtaining 50 - 60 g/cbm yield with a maximum catalyst life of 4 - 6 weeks.

Franz Fischer and Ackermann ^{10/} have obtained in 1936 50 g of liquid hydrocarbons/cbm of mixed gas by following very definite conditions of precipitation of the copper-free catalyst and operating at atmospheric pressure. This yield began to drop off, however, after a few days, and they got less than 40 g during the third week.

The work then was done with a synthesis gas containing carbon monoxide and hydrogen in a proportion of 1 : 2, even though it had already been recognized that the conversion of carbon monoxide with iron catalyst proceeded entirely according to the empirical equation.



If the proportion of CO to H_2 in the synthesis gas used was 2 : 1, carbon monoxide was only partly converted, and the activity of the catalysts decreased extraordinarily rapidly.

Yields obtained in work up to this time were at most less than half as great as the yields of the industrial gasoline synthesis with cobalt catalysts, which prevented their introduction into the industry.

The present work is a report of means found recently of obtaining an almost complete utilization of a carbon monoxide-hydrogen mixture at a slightly increased pressure over extraordinarily long periods of time by a proper pretreatment of the iron catalyst. Different relative proportions of paraffin, gasoline and gasol hydrocarbons are formed depending on operating conditions. The total yields of this so called "iron middle pressure synthesis" is as great as in the synthesis with cobalt catalysts, permitting at present replacing cobalt with iron.

Towards the end of 1937 Dr. Fischer has already reported on the favorable course in our work on the synthesis with iron catalysts. It was intended at that time to give the opportunity to representatives of gasoline synthesis to verify rapidly in their laboratories the results obtained by us. The importance of replacing cobalt with iron in the synthesis was particularly great in Germany, and Dr. Fischer and myself and a number of collaborators have intensely followed up the work in this field in the meantime and in particular during the last year.

Patents on the important results published in the present paper have been applied for by us in the name of the Society for Study and Utilization (Studien- und Verwertungs - Gesellschaft). Applications dating back to 1937 have been turned over to the Ruhrchemie A.G. to apply for joint patents. In the meantime corresponding patents have also been obtained and published in a number of foreign countries.