TOM Reel 101, Doc. PG-21578-NID
"THE MIDDLE-PRESSURE SYNTHESIS WITH IRON CATALYSTS, SEPTEMBER 9, 1939"

INTRODUCTION*

Some time ago we published a piece of work under the title, "How Closely can the Fischer-Pichler Middle-Pressure Synthesis[4] Approach the Theoretically Possible Yields." The experiments were carried out with cobalt-thorium catalysts. The yields of solid and liquid hydrocarbons (excluding gasol) amounted to approximately 170 grams per normal cubic meter of ideal gas. Under the most favorable conditions, this product contained over 50 percent of paraffins.

HISTORICAL DEVELOPMENT

Ever since Franz Fischer and his collaborators carried out the synthesis of hydrocarbons with CO and H_2, the desire was prevalent to substitute the cobalt and thorium by cheaper catalytic agents, which would work in a similar manner and would require approximately the same starting materials. Again and again we resorted to iron catalysts. In 1923, Franz Fischer and H. Tropsch[5] obtained various oxygen-containing organic compounds when they passed water-gas over alkalized iron shavings at pressures of approximately 100 atmospheres and temperatures of between 350-450°C. They termed their product Synthol. Research work of the Badische Anilin und Sodafrabrik[6] in 1913 was carried out at similar pressures and temperatures. In 1925, this

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[4] Fischer, F. and Pichler, H., Brennstoff Chemie <u>20</u>, 221 (1939).

[5] Fischer, F. and Tropsch, H., Brennstoff Chemie <u>4</u>, 276 (1923).

[6] See, for example, Juergen-Schmidt, The Carbon monoxide Akademische Verlagsges, Leipsig, 1935, p. 91.

* The content of this work was communicated to the Studien und Verwertungs-Gesellschaft in 1937. As it has since been published as patent literature in various foreign countries, there is no reason to delay its publication at the present time. (Compare French Patent No. 841043)

work led to the methanol synthesis. Fischer and Zerbe[7] in 1923 showed that alkalized iron shavings used as a catalyst converted CO_2 and H_2 through the intermediate formation of CO and H_2 to oxygen-containing compounds. As the pressure of the reaction was reduced, the amount of hydrocarbons formed increased steadily, whereas the quantity of oxygenated compounds decreased. They worked with a recycling apparatus at a temperature of 410°C. and at 100 atmospheres pressure and lower. At 7 atmospheres, the oil contained 40 percent of products insoluble in concentrated sulfuric acid. These products were of petroleum character.

In 1926, Fischer and Tropsch[8] revealed that the petroleum synthesis could also be carried out with iron catalysts at temperatures of around 300°C. when using CO and H_2 at atmospheric pressure. Under such conditions, hydrocarbons were formed. It was attempted by modification of the synthesis conditions as well as by the addition of promoters to the catalyst to increase the activity of the iron catalysts. Lowering the reaction temperature was also attempted in order to increase the yields of liquid hydrocarbons. In 1928[9] the yields at atmospheric pressure were approximately 30 to 40 grams of benzine and oil per cubic meter of water-gas. The temperatures could be lowered to 240-250°C. The lifetime of the catalyst was only a few days.

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[7] Fischer, F. and Zerbe, Z., Conversion of Coal into Oil: Verlag Gebr. Borntraeger, Berlin 1924, p. 320.

[8] Fischer, F. and Tropsch, H., Brennstoff Chemie 7, 97 (1926).

[9] Fischer, F. and Tropsch, H., Ges. Abhandlungen zur Kenntnis der Kohle 10, 313 (1930)

Fischer and Tropsch[10] had attempted in 1927 to convert water-gas at 10-15 atmospheres pressure and 250-280° C., using iron-copper catalysts which were produced by the decomposition of the nitrates. These catalysts were taken into operation with water-gas immediately. Their reaction products consisted of aqueous and oily substances appearing in the ratio of 3:2 to 1:1. At this time, the authors indicated that the yields obtained at elevated pressures were smaller than the yields at atmospheric pressures. In 1934, however, Fischer[11] showed in a lecture on the benzine synthesis that the highest yields obtained with the iron catalysts at atmospheric pressure were 30-35 grams per cubic meter of mixed gas (this corresponds approximately to 40-45 grams per cubic meter of normal CO-H_2 mixture). He added, however, that this initial yield decreased by 20 percent within 8 days.

Fischer and Meyer[12] endeavored in 1934 to 1936 to increase the activity of the iron catalysts, and thereby increase the yields of liquid hydrocarbons. When they used iron-copper precipitated catalysts, they succeeded in obtaining 50-60 grams per cubic meter of products at atmospheric pressure with a maximum catalyst lifetime of 4 to 6 weeks.

Fischer and Ackermann[13] obtained 50 grams of liquid hydrocarbons in 1936 when they used a precipitated copper-free catalyst. Their working pressure was atmospheric. This yield, however, decreased to 40 grams after only 3 weeks of operation.

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[10] Fischer, F. and Tropsch, H., Brennstoff Chemie 8, 165 (1927).
[11] Fischer, F., Brennstoff Chemie 16, 2 (1935).
[12] Fischer, F. and Meyer, K., unpublished work from the Institute.
[13] Fischer, F. and Ackermann, P., unpublished work from the Institute.

At this time, a synthesis gas was employed which contained CO and H_2 in the ratio of 1:2, although it had been recognized that with iron catalysts the CO conversion goes almost exclusively according to the summary equation:

$$2CO + H_2 = CH_2 + CO_2.$$

If a synthesis gas was used which was composed of $2CO + 1H_2$, the CO was used up only partially and the catalyst activity decreased extraordinarily fast.

The experiments carried out so far indicate that the maximum yields obtained up to this time were approximately half those from cobalt catalyst. Therefore, it was not thought feasible to employ the reaction with iron catalysts on a commercial scale.

RESULTS OF THE PRESENT STUDY

It is the object of the present work to point out that iron catalysts which are properly pretreated and which are operated at slightly elevated pressures are capable of converting a theoretical mixture of CO and H_2 into hydrocarbons over a very long period of time. By this synthesis, predominantly benzine and valuable gasol hydrocarbons are formed. The total yields are of the order of magnitude one is accustomed to see in connection with cobalt catalysts, so that it appears feasible now to replace cobalt by iron in industry.

ARRANGEMENT OF THE APPARATUS

The apparatus used was similar to that employed for the middle-pressure synthesis with cobalt catalysts. It has been described repeatedly and diagrams have been given frequently[14/15/]. For the laboratory experiments,

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[14/] Fischer, F. and Pichler, H., work cited in footnote 4.

[15/] Fischer, F. and Pichler, H., Brennstoff Chemie 20, 42 (1939).

the catalyst tubes were built into aluminum block furnaces, and were arranged in positions slightly inclined from the horizontal. The length of the catalyst layer was approximately 30 cm., and contained an equivalent of 10 grams of Fe. Over this catalyst was passed 4 liters of synthesis gas (referred to one atmosphere pressure) per hour. The low-boiling benzine fractions and gasol hydrocarbons which formed during the synthesis and were not condensed in the receiver were adsorbed by activated charcoal and later recovered.

PREPARATION OF THE CATALYST

Methods of Preparation

At first we were of the opinion that variations in the catalyst preparation or additions to the catalyst would cause an increase in the yields of liquid hydrocarbons. We manufactured several hundred iron catalysts, starting from ferrous as well as ferric salts. The catalysts were prepared by various precipitants such as soda or ammonia, as well as by nitrate decomposition. We used carriers and fillers. We prepared catalysts which did not contain copper and others which contained copper, as it was known from previous experiments that the addition of copper allows the use of lower reaction temperature. The precipitations were carried out at various temperatures and various rates. The precipitates had entirely different crystalline structures and magnetic properties.

In the course of our work, we discovered that satisfactory results can be obtained with different iron catalysts provided they were pretreated with a CO-containing gas prior to operation under pressure.

Standard Catalyst

Our standard catalyst was precipitated from hot iron nitrate solution by soda. Aside from a few tenths of a percent of alkali which the catalyst contained, the residual component consisted of pure iron. The dried and perhaps pelleted iron precipitate was treated with CO-rich gas, or better still, with CO alone at temperatures of about 250°C. The time of induction lasted 24 hours at atmospheric pressure, or at pressures which were essentially lower than the operating pressure. During this pretreatment, which we called "Formierung" not only a reduction was effected (with H_2 no effect could be noticed), but carbon was deposited in the crystalline lattice as well.

With respect to the catalyst question, it should be mentioned that an iron catalyst which was not pretreated is not capable of converting a stoichiometric $CO-H_2$ mixture completely into hydrocarbons at atmospheric pressure nor even 10 atmospheres. However, it can convert this gas mixture for many months when it was pretreated at low pressures and taken into operation at high pressures.

THE SYNTHESIS GAS

It was mentioned above that the conversion of CO and H_2 with iron catalysts at atmospheric pressure proceeds almost exclusively according to the equation: $2CO + H_2 = CH_2 + CO_2$. We have found that at elevated pressures and with increased H_2 content in the initial gas, the reaction $CO + 2H_2 = CH_2 + H_2O$ appears to become more prevalent. The theoretical ratio of CO to H_2 at 15 atmospheres is about 1.5:1.

This gas was produced in the ordinary water-gas generator of the Institute. Steam and CO_2 were passed simultaneously over incandescent coke, the reaction proceeding according to the equation: $5C + 4H_2O + CO_2 = 6CO + 4H_2$. The CO_2 present in 50-60 percent concentration in the end-gas was scrubbed out and returned to the synthesis gas generator for the production of $CO + H_2$.

PRESSURE AND TEMPERATURE VARIATIONS

It was pointed out that the iron catalysts were inducted above 250°C at pressures lower than the operating pressure. This was best accomplished in a separate apparatus. After pretreatment, the catalyst was taken into operation with synthesis gas at elevated pressures. We found that at pressures below 5 atmospheres, the conversion of the CO was incomplete, while at 10-20 atmospheres, best yields were obtained. At this pressure, the optimum working temperatures were 230-240°C. Increasing the operating pressure above 20 atmospheres necessitates raising the operating temperature. However, the reaction temperature should be kept as low as possible if water is the cooling liquid. Otherwise, very heavily walled apparatus becomes necessary in order to withstand high steam pressures.

The synthesis with iron catalysts is much less sensitive with respect to temperature variations than is the synthesis with cobalt.

DURABILITY OF THE CATALYSTS

It has been said that at atmospheric pressure the lifetime of the iron catalysts is 4-6 weeks. In the middle-pressure synthesis, however, the lifetime of the iron catalysts seems to be many times greater; indeed, the activity remains constant indefinitely.

Figures 1 and 2 show the development of the synthesis with iron catalysts. Figure 1 shows the variation of contraction with length of time of operation. For these experiments, the temperature was always regulated in such a way as to yield a maximum gas contraction. Curve 1 shows the optimum conditions when working with mixed gas ($CO:H_2 = 1:2$) at atmospheric pressure. When the synthesis was carried out with a gas which was richer in CO ($CO:H_2 = 3:2$), the contraction quickly decreased after it had reached a value of 38 percent (Curve 2). Curve 3 shows the results obtained with a

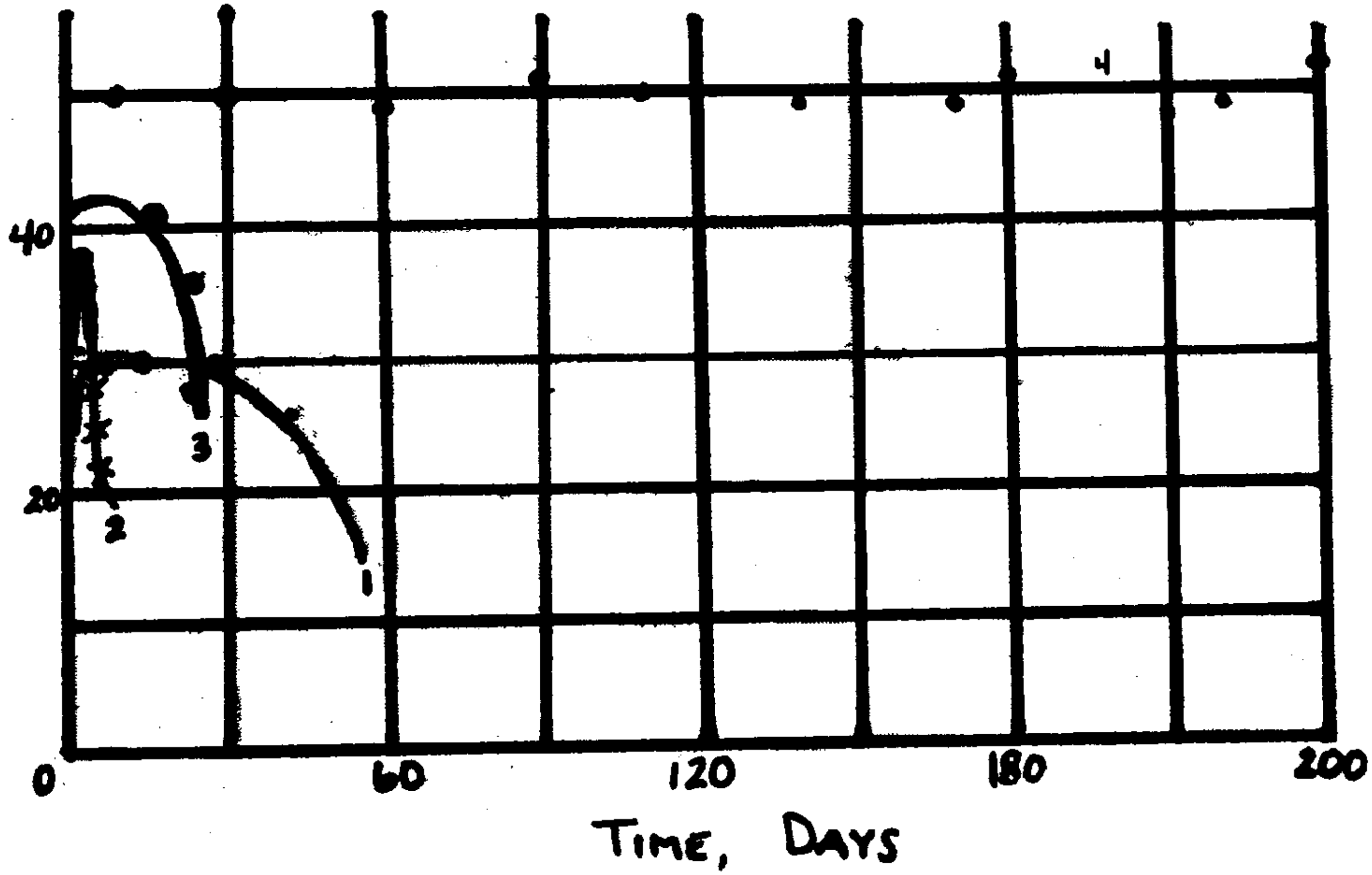

Figure 1 - Variation of contraction with time.

theoretical gas mixture at 15 atmospheres pressure. The catalyst in this experiment was not previously inducted. Complete conversion was not obtained, and the activity of the catalyst decreased comparatively quickly. Curve 4 shows the relationships for the iron middle-pressure synthesis. In this case, the catalyst was pretreated at a pressure lower than 15 atmospheres, and the synthesis operated with a theoretical gas mixture at 15 atmospheres. Even after 8 months of operation, the conversion remained practically complete.

Figure 2 shows the increase in operating temperature with time versus maximum yields. All three curves refer to the iron middle-pressure synthesis and cover information on the development of the past two years. Any regeneration or reactivation of the catalyst was omitted. Experiment 1 was started on September 1, 1937, Experiment 2, in December 1938, and Experiment 3 has been running since March 1939. During Experiment 1, where an iron-copper catalyst was used, it was necessary in the first three months of operation to increase the temperature by 40°C, in order to keep the conversion constant. In Experiment 2, an unpromoted iron catalyst was used. In this case, the temperature rise for the first three months was 27 degrees, and only 10 degrees for the next five months. In Experiment 3, no temperature increase was necessary for the first four months of operation. The conversion remained absolutely constant. The unpromoted iron catalyst which was used for this experiment differs from the one in Experiment 2 by the mode of pretreatment.

REACTION PRODUCTS

Yields

Table 1 shows the yields of Experiment 2 (corresponding to curve 2 of Figure 2 after 100 and 200 days of operation). The yields amounted to 130-133 grams per normal cubic meter of nitrogen-free CO-H_2 mixtures. 41 to

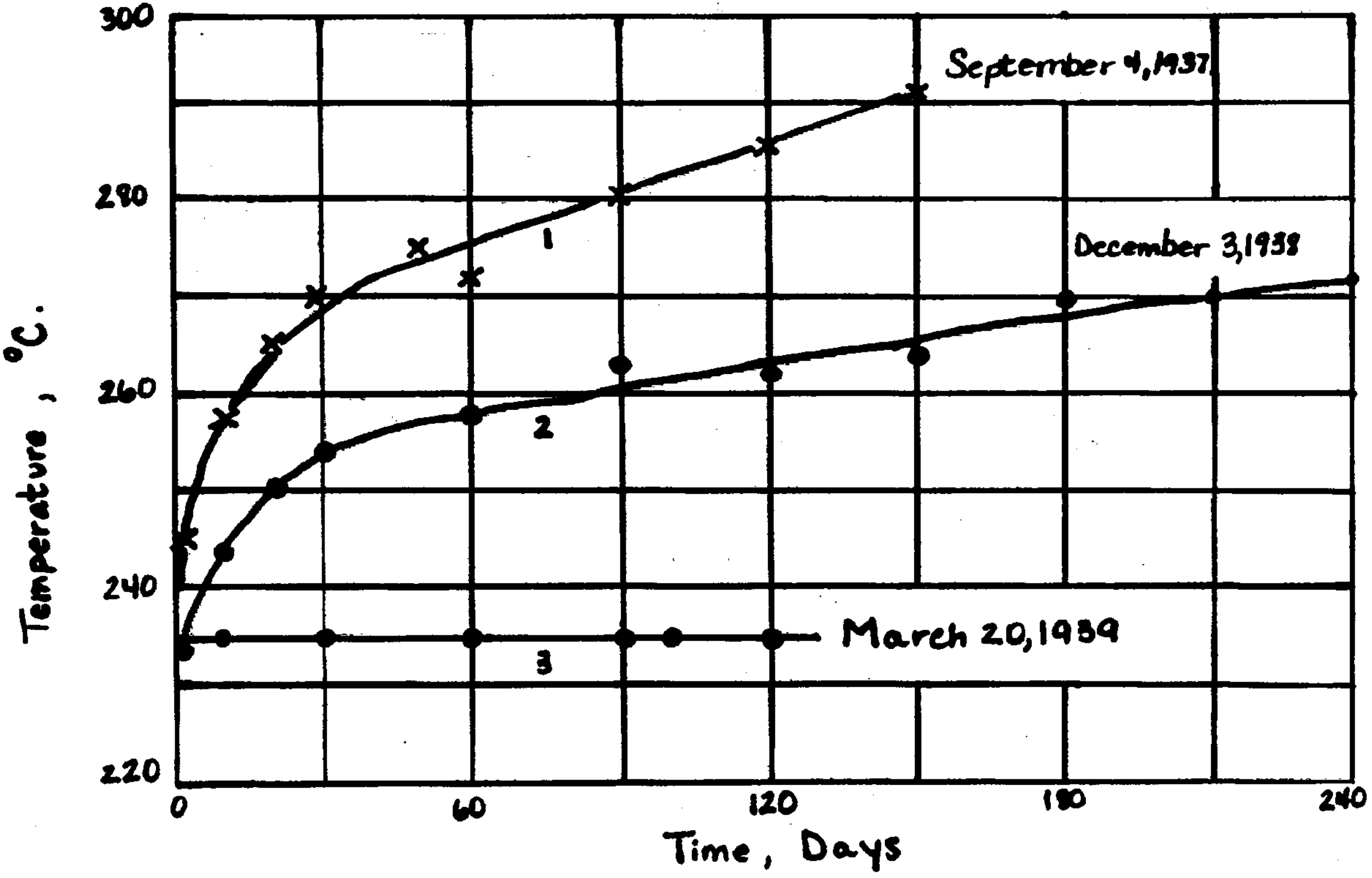

Figure 2 - Variation of temperature with time.

42 Percent of this yield was condensed in the pressure receiver of the synthesis apparatus; 28-29 percent consisted of benzine adsorbed on activated charcoal; 22-23, saturated hydrocarbons; and 7-8, unsaturated C_3+C_4 hydrocarbons.

Table 2 gives the yields of Experiment 3 (corresponding to curve 3 of Figure 2 after 40, 70, and 100 days of operation). In this experiment the yields were higher than 150 grams per normal cubic meter of gas. 70 Percent of the yield consisted of liquid hydrocarbons, 30 percent of gasol hydrocarbons. Roughly, one-half of the latter fraction was unsaturated.

Table 1.- Yields of Experiment 2

Days of operation	Temp., °C.	Solid, liquid, and gasol (C_3+C_4) hydrocarbons g./Nm^3	Percent of Total Yield: Condensed hydrocarbons	Activated carbon benzine	C_3 + C_4 hydrocarbons: Saturated	Unsaturated
100	263	133	41	29	23	7
200	271	130	42	28	22	8

Table 2.- Yields of Experiment 3

Days of operation	Temp., °C.	Solid, liquid, and gasol (C_3+C_4) hydrocarbons g./Nm^3	Percent of Total Yield: Condensed hydrocarbons	Activated carbon benzine	C_3 + C_4 hydrocarbons: Saturated	Unsaturated
40	235	150	53	18	14	15
70	235	155	52	18	16	14
100	235	156	50	20	13	17

Nature of Reaction Products

The liquid hydrocarbons contain approximately 66 percent of a benzine fraction which boils below 180°C., and 20 percent which boils between 180-300°C. The content of solid paraffin in the product is approximately 5 percent, as determined by the butanone method. By extraction of the catalyst it is possible to get paraffins which have a melting point up to 125°C.

In general, 2/3 of the benzine fraction consists of unsaturated compounds, and 1/3 of saturated hydrocarbons. The density of the benzine is approximately 0.7 at 15°C. The octane number (IG-test engine) of the neutral, stabilized, but otherwise untreated benzine boiling up to 180°C. is about 60.

If the gases issuing from the iron catalyst chamber (consisting mainly of gasol and benzine vapors) are passed over a phosphoric acid catalyst, at the same pressure and at constant temperature, a partial polymerization of the unsaturated hydrocarbons occurs. The benzine fraction thus obtained which boiled below 180°C., after washing and stabilizing, had an octane number of 67. If 0.7 cc. of lead tetra ethyl was added per liter, the octane number of the benzine increased 10 points, to 77. If a benzine fraction boiling below 150°C. (56 percent of the total liquid product formed) was treated with 0.8 cc. of lead tetra ethyl per liter, the octane number was increased to 80.

If the CO_2 is removed from the reaction gas before polymerization is carried out, and if polymerization occurs under optimum conditions, a more valuable benzine can be obtained.

The end-gas which is obtained after the gasol has been removed contains approximately 50-60 percent CO_2. It has been pointed out above that this CO_2 is converted to synthesis gas in the gas generator. If not only the CO_2, but the other gases such as methane, CO, and H_2, present in the end-gas, are returned to the gas generator, the total yield per cubic meter of synthesis gas can be increased by 10-20 percent.

SUMMARY

A procedure has been described which converts CO and H_2 into valuable hydrocarbons, and instead of cobalt-thorium catalysts, employs iron catalysts, which except for traces of alkali, do not contain additional material. Before these catalysts can be used, however, they must be inducted at a certain pressure and temperature with CO or CO-containing gases. The synthesis proper is best carried out at pressures between 10-20 atmospheres with an initial gas which contains CO and H_2 in a ratio of 3:2.

Without regeneration or reactivation of the iron catalyst, constant yields of 150 grams of liquid, gasol (C_3+C_4), and solid hydrocarbons per normal cubic meter of synthesis gas are obtained indefinitely.

The crude benzine which represents the greatest portion of the reaction products is comparatively knock-proof. This is on account of its high unsaturated content. The primary products from iron catalysts contain more unsaturated compounds than those from cobalt catalysts. The benzine may be materially improved by following the synthesis with a polymerization step, which results in partial polymerization of the primary unsaturated hydrocarbons and marked improvement in the quality of the benzine.

For the experimental work done we are grateful to Messrs. Dienst, Lohmar, and Meusel, and especially Ruckensteiner.

"MIDDLE-PRESSURE SYNTHESIS WITH IRON CATALYSTS" (A Summary)

INTRODUCTION

In September 1940, a lecture was given at the Kaiser-Wilhelm Institute for Coal Research at Muelheim-Ruhr on the subject of the middle-pressure synthesis on iron catalysts. The content of the lecture was reported.

At the time the lecture was delivered, we desired to install synthesis equipment which was designed to utilize iron catalysts. At this time we were motivated by the one aim of obtaining maximum yields of benzine, paraffin, and gasol hydrocarbons even if it were necessary to increase the reaction temperature above that of the cobalt middle-pressure synthesis.

Recently, it has been planned to modify the existing equipment for use with iron catalysts. This newest aim, however, excludes the employment of temperatures above 225°C. and as far as the middle-pressure synthesis units are concerned, any operation carried out at pressures of above 10 atmospheres should be avoided.

FACTORS INFLUENCING THE SYNTHESIS AT LOWER TEMPERATURES

From research work at the Muelheim Institute for Coal Research, we have learned that the following factors must be considered if it is desired to work with iron catalysts at lower temperatures.

Catalyst

It is necessary to use a very active catalyst. Such a catalyst can be obtained by precipitating iron-salt solutions. The addition of small amounts of copper as, for instance, one percent or less on the basis of the iron content and small quantities of alkali as, for instance, ¼ percent as referred to the iron, are desirable to enhance catalyst activity.

Induction of the Catalyst

A certain proper pretreatment of the catalyst is required (induction of the catalyst). This induction is most advantageously carried out by using CO-rich gases at low pressures and at higher-than-synthesis temperature. (This process is analogous to the reduction procedure which is given to cobalt catalysts. It is recommended that this step be carried out in a separate apparatus from the actual synthesis chamber.)

Operating Pressures

The synthesis should be carried out at pressures above atmospheric. It is recommended that an optimum pressure of 8-10 atmospheres be observed.

Synthesis Gas Composition

It is recommended that the synthesis be carried out with a H^2-rich synthesis gas.

If all the recommendations which have been listed in the above four items are observed, it is possible to use iron catalysts for the synthesis of liquid, solid, and gasol hydrocarbons. On can use mixtures of CO and H_2.

below the temperatures indicated above and within the proper pressure limits. Figure 3 shows the variation in reaction temperature with synthesis gas composition, and Figure 4 summarizes graphically hydrocarbon and water yields versus synthesis gas composition, after 4 weeks of operation. (This refers to a one-stage operation.)

When a gas was used which was extremely rich in H_2, as for instance, a mixture of $CO:H_2 = 1:10$, at a pressure of 10 atmospheres and a gas rate of [illegible] liters of end-gas per 10 grams of iron, CO was converted and higher hydrocarbons formed at 130°C. At 140°C., the CO conversion was 38 percent complete with a contraction of 12 percent. When a CO rich synthesis gas was used, the course of the reaction follows a fundamentally different course. Under such conditons, the greatest part of the CO-oxygen is no longer converted to CO_2, but to water.

If one works with a synthesis gas which contains CO and H_2 in the ratio of 1:4, then at a working pressure of 10 atmospheres, the synthesis temperature varies between 180-200°C. Under these conditions, therefore, the temperatures of the synthesis are comparable to those of the cobalt synthesis. The yields of liquid and gasol hydrocarbons per normal cubic meter of ideal gas are approximately 50 grams for the first stage (of which [illegible] percent is gasol). Approximately 82 grams per normal cubic meter (ideal gas) of water is formed also.

REACTION PRODUCTS

By treating the portion which boils up to 180°C. with phosphorous pentoxide-sulfuric acid mixtures, 41 percent could be dissolved out. The gasol fraction contained approximately 40-50 percent of unsaturated hydrocarbons.

When an Engler-distillation was carried out on the liquid and solid products (representing an average of the first four weeks of operation),

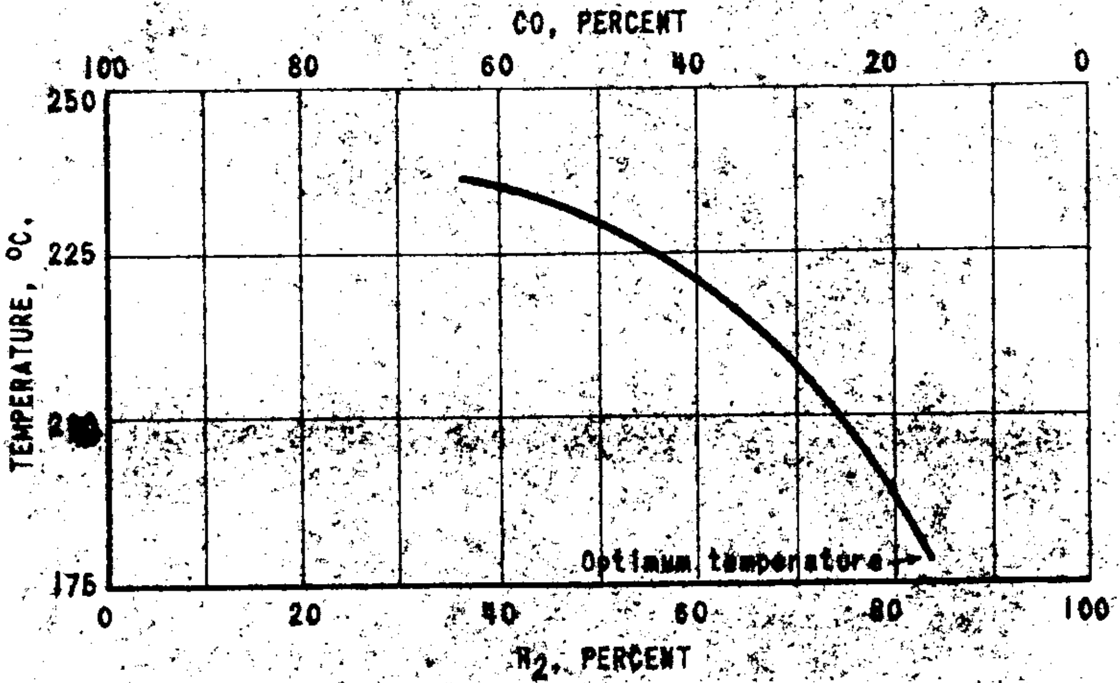

Figure 3. - Variation in temperature with synthesis gas composition.

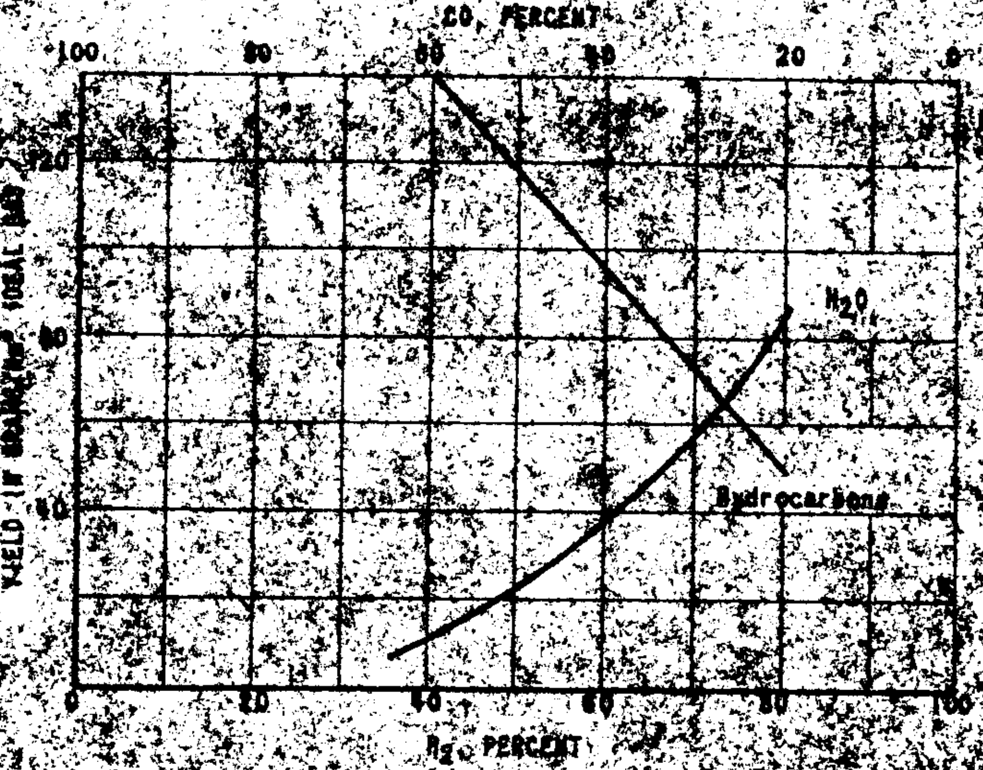

Figure [illegible].- Variation in yield with synthesis gas composition.

X.0 percent was distilled at 48°C, 50 percent at 152°C, and 73 percent at 246°C. Of the higher-boiling constituents determined by the butanone methode, 54 percent consisted of solid paraffins.

In comparison to the cobalt catalysts, the iron catalysts produce reduction products which contain larger quantities of gasol oxygen-containing organic compounds. When the products obtained from a 4H2 + 100 synthesis gas were acetylated, an alcohol content of 20.3 percent was obtained (reported as propyl alcohol).

The reaction water contained traces of methyl alcohol, approximately 1.5 percent ethyl alcohol, 0.8 percent propyl alcohol, and 0.8 percent C4 alcohols.

MULTISTAGE OPERATION

In order to make the process economical, it is necessary to work in several stages (another alternative is to resort to recycling). When working in stages, it might be necessary to replenish CO concentration before each consecutive stage. Thus, using a 2H2 + 1CO gas mixture in two stages at 210°C., it is possible to equal the yields of the cobalt synthesis. If a gas is used which is still richer in H2, the temperature of the conversion may be lowered. However, the higher the H2 content of the gas, the more stages are recommended.