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SYNTHESIS OF HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN

by

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INTRODUCTION

The purpose of the present paper is to present a survey of the process for the production of hydrocarbons from carbon monoxide and hydrogen discovered at the Kaiser Wilhelm Institut für Kohlenforschung, Mülheim-Ruhr, by Franz Fischer and his collaborators, and of the development of this process both at the Institute, and in the laboratories of industrial concerns working in the same field.

Discussion of this work has been organized as follows:

I. General and historical considerations.

II. Synthesis of hydrocarbons from carbon monoxide and hydrogen in the presence of catalysts of the iron group of the periodic system.

III. Synthesis of hydrocarbons in the presence of catalysts of the platinum group.

IV. Synthesis of hydrocarbons in the presence of oxides (isosynthesis).

V. Brief discussion of the mechanism of the hydrogenation of the oxides of carbon.

Particular attention has been given to Part II, which is concerned with work of considerable practical importance at the present time. Of the other sections, some serve to complete the general picture; some are of interest because of the special nature of the products formed, and some because of what they contribute to the study of the general course of the reaction. The present report is concerned with the chemical nature of the materials involved. The technical and industrial aspects of the problem, which will form the subject of a second paper, are not discussed.

The present paper is intended as a rapid survey of the development of the hydrocarbon synthesis and of the most important work connected with it. A complete list of publications on the subject would greatly exceed the scope of this paper. The same is true of a discussion of the possibilities for converting primary synthesis products into gasolines and lubricating oils of higher values. Such a report may form the subject of a later paper. In addition, the reader is referred to the exhaustive discussion of the synthesis literature by H.H. Storch (Chemistry of Coal Utilization, Edited by H.H. Lowry, published by John Wiley and Sons, Inc., New York, 1945, Vol. II, p. 1797).

H. Pichler

PART I
GENERAL AND HISTORICAL CONSIDERATION

1. General Considerations

The purpose of the research discussed in the present paper was the chemical synthesis of a product having the properties of natural petroleum, and prepared from simple materials, readily available for technical purposes. The process was designed to give those countries with insufficient or rapidly dwindling sources of natural petroleum, the means of building up fuel industries from their own resources and eventually enabling them to supply large portions of the organic chemical industry with essential raw materials.

Carbon monoxide and hydrogen appeared to be indicated as starting materials for a synthesis of this type. Their production is largely independent of the nature of the raw materials available in different parts of the earth, either now or at a future time. Natural gas, bituminous and subbituminous coals, lignite, coke, wood, and perhaps even (should these organic raw materials be lacking at some later date) natural carbon dioxide mixed with electrolytic hydrogen, can all be drawn upon to produce a mixture of carbon monoxide and hydrogen for the synthesis.

The primary products formed by synthesis in the work carried out by Franz Fischer and his collaborators at the K.W.I. consisted essentially of saturated and unsaturated liquid aliphatic hydrocarbons. Under certain conditions oxygenated and cyclic compounds were also obtained. These primary synthesis products can be converted by suitable methods to products satisfactory for use as motor fuels. The higher-boiling liquid hydrocarbons constitute an excellent Diesel fuel. The anti-knock rating of the primary gasoline hydrocarbons is not always satisfactory, but treatment by various well-known procedures can convert these products into valuable gasolines. Polymerization of olefins produces a wide variety of lubricating oils. Oxidation of paraffins gives fatty acids to be used as raw materials in the production of soaps, cleaning agents, and industrial and edible fats. Addition of carbon monoxide and hydrogen to olefins produces aldehydes from which all manner of alcohols and acids may be derived. Cyclization of paraffins results in the formation of aromatics, etc. Even the course of the primary synthesis itself can be oriented in any number of different ways, suggesting that perhaps the time is not too distant when carbon monoxide and hydrogen will hold the same all-important place in the domain of industrial organic chemistry, that carbon dioxide and water now occupy in nature. In the presence of solar energy and appropriate catalysts, these raw materials form the essential material of all organic life.

In connection with a farewell address, delivered in 1943 at the Mülheim Institute for Coal Research, Dr. Fischer showed two tables entitled, respectively, "Historical survey of syntheses from carbon monoxide and hydrogen" and "Hydrocarbon synthesis from carbon monoxide and hydrogen." Since these tables published by Franz Fischer correspond to the classification used here, they can have no better place than at the beginning of the present paper.

Table 1.- Historical Survey of Syntheses from Carbon Monoxide and Hydrogen (according to Franz Fischer)[1]

1902	P. Sabatier and J.B. Senderens	CH_4 with nickel from $CO + 3H_2$ or $CO_2 + 4H_2$
1913	BASF D R P 293787 " 295202 " 295203	Process for production of hydrocarbons and derivatives at high pressures from CO and H_2.
Nov. 1922	F. Fischer and H. Tropsch D R P 411216	Synthol, oxygenated hydrocarbon derivatives with alkalized Fe and other catalysts.
Sept. 1923	F. Fischer and H. Tropsch	On the formation and composition of synthol.
July-Sept. 1923	BASF or I.G. D R P 415686 " 441433 " 580695	Methanol patents, Zn-base, exclusion of Fe.
July 1925	F. Fischer and H. Tropsch D R P 484337	Normal pressure synthesis of gasoline.
July 1936	F. Fischer and H. Pichler D R P 731295	Medium pressure synthesis with cobalt.
July 1937	F. Fischer and H. Pichler D R P pending	Medium pressure synthesis with iron.
May 1938	F. Fischer and H. Pichler D R P 705528	High pressure synthesis of high-melting paraffins with ruthenium.
Oct. 1941	F. Fischer, H. Pichler and K.H. Ziesecke D R P pending	Isosynthesis.

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[1] Corresponds to Table 5, F. Fischer, lecture in Oel und Kohle, 1943, No. 21, 22 (June 1st).

Table 2. - Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen[1]

Products	Gas	Liquid	Solid	Catalyst	Pressure atm.	Temp. °C.	Discovered and developed by	
A) CH_4	all	----	----	Ni, Co	1	with Ni 200° C. with Co 300° C.	Sabatier and Senderens	
B) Paraffins & olefins	little	much	little	Ni, Co, Fe	1	with Co 190° C.	KWI	F. Fischer and H. Tropsch
C) Paraffins & few olefins[2]	little	much	much	Co	5-20	190° C.	KWI	F. Fischer and H. Pichler
D) Paraffins & numerous olefins	little	much	little[3]	Fe	5-20	240° C.	KWI	
E) Mainly solid paraffins	"	little	much	Ru	above 100	200° C.	KWI	
F) Isoparaffins	much gasol[4]	much	----	ThO_2	above 100	above 400° C.	KWI	
G) Naphthenes Aromatics	much	much	----	ThO_2	above 100	above 400° C.	KWI	

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[1] Corresponds to Table I, Lecture, F. Fischer, Oel und Kohle, 1943, No. 21, 22 (June 1st).

[2] The olefin content may be increased by use of gases containing excess carbon monoxide (i.e., Recycling experiments of Ruhrchemie and Lurgi).

[3] Can be increased considerably by appropriate choice of conditions.

[4] Mainly isobutane.

2. Earlier Synthetic Processes

A. Synthesis of Methane

Using as starting materials a mixture consisting of 1 part of carbon monoxide and 3 parts of hydrogen, Sabatier and Senderens (1902) were the first to succeed in preparing a carbon-hydrogen compound, namely methane, by catalytic synthesis. The synthesis was carried out at about 200°C. in the presence of nickel, and at about 300°C. in the presence of cobalt. In countries where natural gas (methane) was lacking, the problem of applying this methane synthesis to technical purposes was approached in a number of different ways. However, in every case, difficulties, first of a technical, and later, of an economical nature, arose. In Germany in recent years the possibility of preparing a standard utility gas by partial methanization of water gas has been the subject of considerable discussion. At times of peak load, the scarcity of available utility gas has been marked. Since gaseous hydrocarbons always form as by-products of the hydrocarbon synthesis, and since it is possible to vary the proportions of gaseous and liquid reaction products obtained, it was suggested that the synthetic production of gasoline be combined with the generation of utility gas.

1/ Pichler, H., Brennstoff Chem. 22, 244 (1941).

In connection with methanization, a large number of patents were applied for, particularly by the Ruhrchemie, A.G.

B. Earlier BASF Patents

In 1913 a small number of patent claims for the preparation of hydrocarbons and oxygenated organic compounds were filed by the

Badische Anilin und Sodafabrik. A wide variety of metals, such as nickel, cobalt, iron, manganese, chromium, titanium, osmium, palladium, and zinc, were listed as suitable catalysts. High pressures, generally up to 100 atmospheres or more, and temperatures from 300 to 420°C. were recommended. This work appears to have been interrupted by World War I and not to have been resumed.

C. Synthol Synthesis

The synthesis of the product known as synthol, essentially a mixture of oxygenated compounds, was described by Franz Fischer and H. Tropsch[2] in 1922 and 1923. Alkalized iron filings were used as catalyst for the conversion of water gas at pressures above 100 atmospheres and at temperatures of about 400°C. This process received no technical application. Table 3 gives a list of the compounds found to be present in synthol.

Table 3. - Compounds Present in Synthol

formic acid
acetic acid
propionic acid
isobutyric acid
fatty acids up to C_6

methanol
ethanol
propanol
acetone
methethyl ketone

propionaldehyde
isobutylaldehyde
diethylketone
methylpropyl ketone
alcohols up to C_9
esters

D. Synthesis of Methanol

Almost simultaneously with the work on synthol at the Mülheim Institute for Coal Research, a process was evolved by the BASF or I.G. in which controlled catalytic conversion of carbon monoxide and hydrogen led to the exclusive formation of a specific compound, namely methanol.

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[2] Fischer, F., and Tropsch, H., Ber. Deut. chem. Gesell. 56, 2428 (1923). Brennstoff Chem. 5, 203 and 217 (1924).

The reaction is catalyzed essentially by zinc oxide, which must be free both of metals belonging to the iron group and of alkalies. The pressure must lie between 200 and 300 atmospheres, the temperature between 200 and 350°C. Credit for the process, which has achieved considerable technical importance, goes to M. Pier.

More recent work[3] has shown that when the alkali-free zinc oxide is replaced by an alkalized zinc catalyst, higher alcohols, and especially isobutyl alcohol, are formed in addition to methanol. Table 4 gives a typical analysis of the so-called isobutyl oil process.

Table 4. - Composition of "Crude Isobutyl Oils"

dimethyl ether	3.0 percent
first runnings	0.2
methanol	51.0
C_1-C_2 fraction	0.4
propanol (first runnings)	0.5
propanol, crude	1.0
isobutyl alcohol, crude	11.0
isobutyl alcohol (second runnings)	0.5
isoamyl alcohol	1.1
higher boiling first runnings	0.1
higher boiling alcohols (145-163°C.)	2.8
fraction 160-200°C.	1.0
fraction 200-270°C.	0.75
residue above 270°C.	0.15
fraction 95-110°C.	0.25
isobutyrone	0.8
residue	0.3
water and losses	24.15

Also very small amounts of propylene, di-isobutylene, propylcyclohexane, and tri-isobutylene.

3. Considerations on the Synthesis Gas Used for the Production of Hydrocarbons

The synthesis of hydrocarbons from carbon monoxide and hydrogen by the process discovered by Franz Fischer[4] and his collaborators proceeds

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[3] Hanisch, I.G. Leuna, TOM Reel 134, Section V, Item 2.

[4] Fischer, F., Pichler, H., and Reder, R., Brennstoff Chem. 13, 421 (1932).

[5] Storch, H.H., see Introduction.

according to the general equations:

$$1)\ n\,CO + 2n\,H_2 = (CH_2)_n + n\,H_2O$$
$$2)\ 2n\,CO + n\,H_2 = (CH_2)_n + n\,CO_2$$

Depending on the reaction conditions, the conversion is characterized by the predominance of summation formula 1) or 2); the proportions in which hydrogen reacts with carbon monoxide vary. In most instances, the best yields are obtained when the ratio of carbon monoxide to hydrogen in the synthesis gas corresponds to that in which they react in the course of the synthesis. However, when special effects are desired, it may be preferable for the carbon monoxide-hydrogen ratio in the synthesis gas to differ appreciably from the ratio in which they react (e.g., excess carbon monoxide for the production of olefins in the cobalt medium pressure synthesis, or excess hydrogen, making it possible to operate at lower temperatures in the iron medium pressure synthesis).

It is not our purpose to discuss here the various technical possibilities in connection with the preparation of water gas. As a rule, technical water gas contains carbon monoxide and hydrogen in a ratio of 1:1.2. When necessary, as for instance in the cobalt catalyst synthesis, a gas having a higher hydrogen content may be obtained by treating a portion of the gas stream according to the equation

$$3)\ CO + H_2O = CO_2 + H_2$$

in the presence of simple catalysts (usually iron-chromium). It is also possible, by converting coke with steam in the presence of coke oven gas, to prepare a hydrogen-rich gas directly at the same time as methane is converted. Carbon monoxide-rich gases may be prepared in the presence of gases containing carbon dioxide.

6/ Fischer, F., Pichler, H., and Kölbel, H., Brennstoff Chem. 16, 331, 401 (1935).

At 1300-1400°C., methane reacts with steam and oxygen in the presence of ceramic materials, according to equations 4) and 5).

$$4)\quad CH_4 + H_2O = CO + 3H_2$$

$$5)\quad CH_4 + 1/2\ O_2 = CO + 2H_2$$

In the presence of nickel or cobalt catalysts, reaction 4) takes place at 900-950°C. Carbon monoxide-rich gases are obtained by reaction of methane with carbon dioxide, possibly from the tail gas of the iron synthesis.

$$6)\quad CH_4 + CO_2 = 2CO + 2H_2$$

Incomplete combustion of methane over a short interval of heating can be controlled in such a way that in addition to a synthesis gas containing 1 CO + 2H2, acetylene is obtained according to equation 7).

$$7)\quad 5CH_4 + 3O_2 = C_2H_2 + 3CO + 6H_2 + 3H_2O + 136\ \text{kcal}$$

The interesting feature of a procedure of this type would lie in the fact that acetylene can be converted simultaneously with carbon monoxide and hydrogen, in the presence of a synthesis catalyst.

The life of catalysts having a cobalt, nickel, or iron base, as well as those of ruthenium, depends to a considerable extent on the absence of sulfur compounds in the synthesis gas. Oxide catalysts, of the type used in connection with isosynthesis, are not affected by sulfur compounds.

7/ Fischer, F., and Tropsch, H., Brennstoff Chem. 9, No. 3 (1928).
8/ Hawk, Golden, Storch, and Fieldner, Ind. and Eng. Chem. 29, 23 (1932).
9/ Natta-Pontelli, Chemica & Industria 19, 177 (1937).
10/ Storch and Fieldner, Mech. Eng., 61, 605 (1939).

11/ Fischer, F., and Pichler, H., Brennstoff Chem. 11, 501 (1930)
DRP 553,178.

Hydrogen sulfide is removed from the gas in the usual manner by purification with bog-iron ore. Organic sulfur is removed at high temperatures in the presence of alkalized iron catalysts, according to a process developed at the Mülheim Institute for Coal Research by Rölen and Feisst[12] known as "Feinreinigung" or Heissreinigung". The details of the procedure depend largely on the nature of the sulfur compounds present and consequently on the previous history of the gas to be purified. The sulfur content of the synthesis gas must not exceed 0.2 to 0.3 grams per 100 cubic meters and should, if possible, be less. It must be checked constantly.

It is also important that the synthesis gas be free of resin-forming substances. Substances of this type do not generally occur in the standard water gas obtained from coke. In the case of gas derived from coal, ~~they must~~ be destroyed by cracking, or removed with active charcoal.

4. Considerations on the Apparatus Used in Synthesis Experiments

The conversion of carbon monoxide and hydrogen to higher hydrocarbons is known to be a highly exothermic reaction. Approximately 700 kilocalories, in other words, more than 20 percent of the heat of combustion of ~~the~~ gas, are liberated for every normal cubic meter of carbon monoxide - hydrogen mixture that reacts. This quantity of heat must be removed from the catalyst chamber, since any increase in the temperature of the catalyst gives rise to undesirable secondary reactions, to increased formation of gaseous hydrocarbons, especially of methane,

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[12] Rölen and Feisst, Brennstoff Chem. 15, 187 (1934).

and to the formation of carbon. The smaller the temperature drop in the catalyst bed, the easier it is to obtain maximum yields of higher hydrocarbons.

With laboratory apparatus of the type used in small-scale experiments, the removal of heat from the reaction zone does not constitute a problem. Thermal radiation from small apparatus is such that in order to maintain a constant reaction temperature, heat must be supplied to the system from without. However, even on a laboratory scale when fixed catalyst beds are used, the thickness of the catalyst layer or the inner diameter of the reaction tube must be determined by the prevailing technical conditions, in order to avoid overheating within the catalyst. In general, the reaction tubes used had an inside diameter of 10 to 12 millimeters. When fixed catalyst beds are employed, the use of reaction tubes with an inside diameter of 20 millimeters or more produces unfavorable results, even in small-scale experiments.

In medium-pressure synthesis, standard iron tubes can be used, whereas in isosynthesis, the tubes must either be made of stainless steel, or of iron lined with copper.

In the fundamental laboratory experiments, the reaction was carried out with a single pass of synthesis gas over a fixed catalyst bed. However, the synthesis can be run in a great number of different ways. As early as 1930-1935, pilot plant experiments with moving catalysts were carried out at the Mülheim Institute. These were known as "sump phase" experiments, in which the catalyst was suspended in heavy oil. There was a fluidized operation in which dry catalyst was circulated through reaction zone, etc. Recycling of gas was also used in the early stages of synthetic development ("recycling experiments").

For economic reasons, these procedures were not continued in the normal pressure synthesis of that time.

In most of the small-scale experiments with fixed catalyst beds involving a throughput of 4 to 10 liters per hour of synthesis gas in the normal- and medium-pressure processes, and 10 to 500 liters per hour in the isosynthesis, the reaction tubes were placed in aluminum blocks heated externally (usually with gas). For normal- and medium-pressure synthesis, laboratory apparatus was also used in which the reaction tubes were kept at the desired temperature by means of water under pressure or oil. At higher temperature the water under pressure was replaced by high-boiling materials such as melted salts like nitrate-nitrite melts, or by diphenyl-diphenyl-oxide. The temperature was kept constant by suitable temperature controls.

Figure 1 gives a diagram of a water-cooled laboratory-scale synthesis apparatus of the type used in different sizes at Mülheim. A diagram of the apparatus used at Schwarzheide for comparative experiments is also given (see medium-pressure synthesis in presence of iron catalysts).

Every effort was made to carry out the pilot plant experiments under conditions approximating those applied in industry. For this reason, in the comparative experiments with iron catalysts at Schwarzheide, discussed in detail in the present work, as well as in experiments at the Mülheim Institute for Coal Research, double medium-pressure reactors were used (distance, 10 mm; catalyst volume, 4.8 liters), whose dimensions and method of heat transfer corresponded to the reactors used in large-scale apparatus (Alberts-Mannesmann model).

A. KWI Apparatus

B. Appa tus used in Schwarzheide tests.

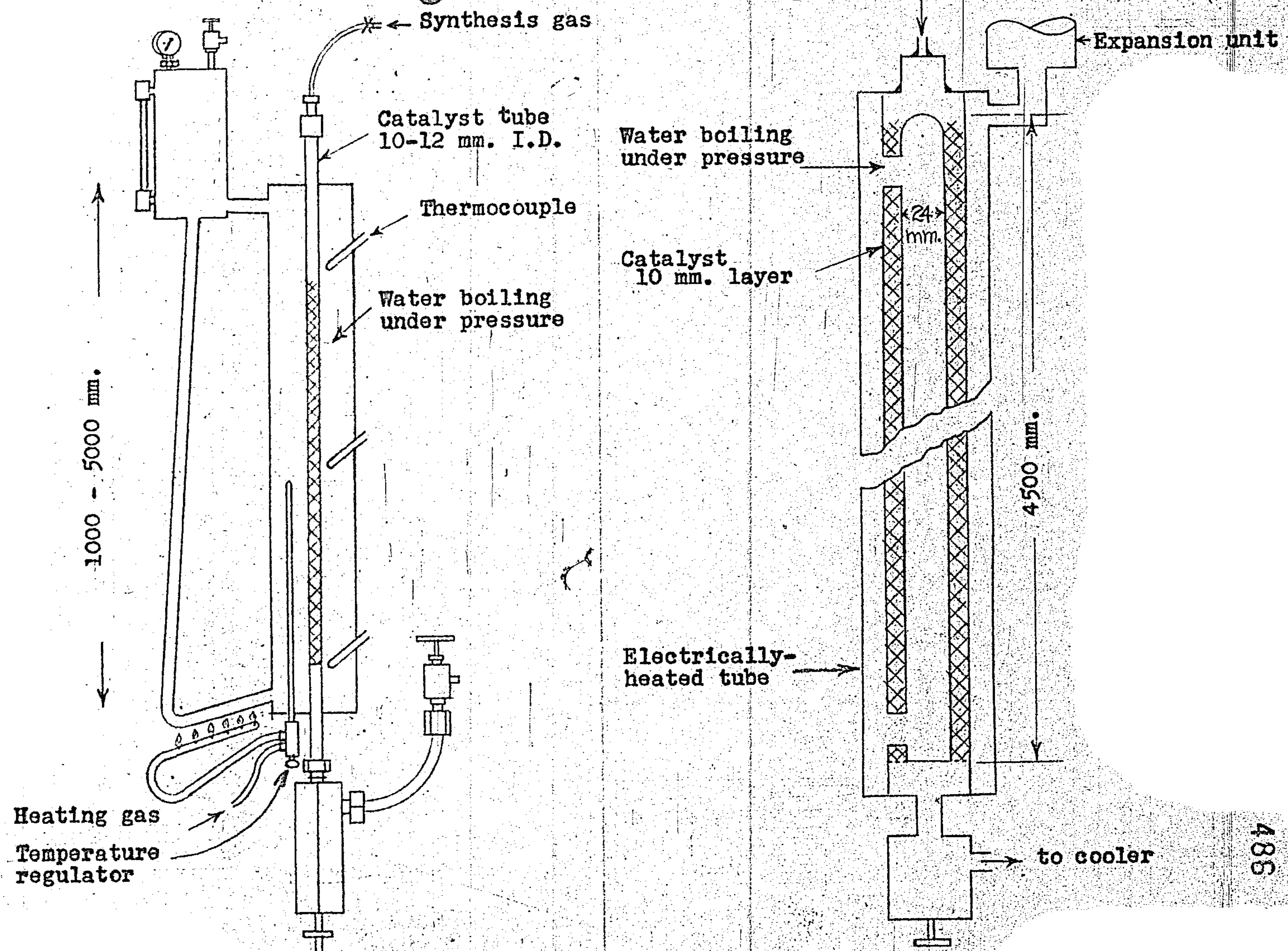

Figure 1: Laboratory synthesis Apparatus

PART II
SYNTHESES OF HYDROCARBONS IN PRESENCE OF CATALYSTS OF THE IRON GROUP OF THE PERIODIC SYSTEM

1. Normal Pressure Synthesis

A. Development in the Laboratory

In 1925, Franz Fischer and Hans Tropsch[13] observed that with sufficiently active catalysts belonging to the iron group, carbon monoxide and hydrogen react at temperatures below 300°C. even at atmospheric pressure.

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[13] Fischer, F., and Tropsch, H., Ber. Deut. chem. Gesell. 59, 830, 832, 923 (1926).

The reaction products obtained under these conditions consist almost exclusively of saturated and unsaturated aliphatic hydrocarbons, from methane to solid paraffins. Cobalt or iron was used as the basic catalyst metal, whereas nickel, due to its high hydrogenating ability, was essentially a methanization catalyst. The catalysts were prepared by decomposition of the metallic salts, and later also by precipitation. It was found that certain oxides, in particular chromium oxide, zinc oxide, beryllium oxide, certain rare earths, uranium oxide, silicic acid, aluminum oxide, magnesium oxide, and manganese oxide, have the property of promoting the activity of the original catalytic metal. Ceramic materials, asbestos, clay chips, pumice stone and activated charcoal were used as catalyst carriers. The necessity of alkalizing iron catalysts and the importance of preliminary reduction of the catalyst, soon became apparent. Nevertheless, the path traveled from the discovery of the first drops of oil formed by the hydrogenation of carbon monoxide to the process in industrial use was a long one.

When in 1928 Hans Tropsch, Franz Fischer's collaborator and the co-discoverer of normal pressure synthesis, left Mülheim to become the director of a new Institute for Coal Research at Prague, the yield obtained by a single pass of synthesis gas over iron and cobalt catalysts amounted to about 20 grams of liquid hydrocarbons per cubic meter of gas[14].

The life of the iron catalysts was 8 days, that of the cobalt catalysts, a few weeks. Step by step, the efficiency of the catalysts was improved by empirical methods. At times it seemed as though the process could find no possible technical application. The introduction of catalysts prepared by precipitation of cobalt or nickel on kieselguhr constituted a decisive step forward and a notable increase in the technical importance of the process. This was the first instance in which appreciable amounts of liquid products were synthesized over a nickel catalyst.

The introduction of the precipitated cobalt catalyst produced an increase in yield: 110 grams per cubic meter of synthesis gas, as against 70 grams previously obtained.

Results of both of these investigations[15, 16] indicate the importance of thorium oxide as a promoter and the necessity of precipitating the catalyst as the carbonate. Calculating on a basis of

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[14] Fischer, F., Brennstoff Chem. 11, 489 (1930).

[15] Fischer, F., and Meyer, K., Brennstoff Chem. 12, 225 (1931).

[16] Fischer, F., and Koch, H., Brennstoff Chem. 13, 61 (1932).

1 normal cubic meter of carbon monoxide and hydrogen mixture and adding to the yield 10 grams of gasol ($C_3 + C_4$), the 110-gram yield mentioned above corresponds with the usual yield of about 145 grams which is still obtained by a single stage synthesis in the presence of cobalt catalysts.

A standard cobalt catalyst (100 Co: 18 ThO_2: 100 Kg) was obtained as follows:

Two solutions were prepared:

Solution 1: 1000 Grams of cobalt and 180 grams of thorium oxide, as the nitrate, were dissolved in 20 liters of distilled water.

Solution 2: 2160 Grams of sodium carbonate were dissolved in 30 liters of distilled water. Shortly before using, 1000 grams of kieselguhr were added to the solution. (On a large scale, precipitation was carried out with 103 grams of sodium carbonate per liter of solution and kieselguhr added with stirring immediately after precipitation).

Both solutions were heated to boiling, and solution 2 (containing the kieselguhr) was poured as rapidly as possible into solution 1. This was then heated to boiling for 1 minute and filtered. The catalyst cake was washed 6-8 times with 20 liters of boiling distilled water (until alkali-free), dried at 110°C., and granulated.

The reduction of the catalyst was effected in the laboratory by passing 20 liters of dry hydrogen per hour per 10 grams of cobalt over catalyst beds 30 centimeters deep. At a temperature of 365°C. it was found that reduction could be stopped after 4-1/2 to 5 hours. Particularly active catalysts are obtained (high degree of reduction) when reduction is prolonged for 20 hours. (On the subject of reduction in technical operations, see pp. 19 and 20.)

The corresponding nickel catalyst (100 Ni : 18 ThO$_2$: 100 Kg) was prepared in a similar manner. Precipitation was carried out with potassium carbonate at room temperature, and the precipitated solution then heated for a short time to boiling (1 minute). The reduction required higher temperatures than those used for cobalt catalysts. Twenty liters of dry hydrogen per hour per 10 grams of nickel was passed at 450°C. for a period of 5 to 20 hours.

The so-called standard nickel catalyst, which has proved extremely useful in hydrogenation, contains 100 grams of nickel, 20 grams of manganese, 10 grams of aluminum oxide, and 100 grams of kieselguhr. In preparing this catalyst, a quantity of nitrate equivalent to 50 grams of nickel was dissolved in 1 liter of distilled water. Potassium carbonate was the precipitant (210 grams of potassium carbonate in 1500 cubic centimeters of water plus 50 grams of kieselguhr). Both solutions were heated to boiling and the precipitate obtained by pouring the potassium carbonate solution into the nitrate solution, with stirring. Drying and reduction were carried out as in the case of the Ni-Th catalysts.

Addition of ammonia to the hydrogen used in reduction enhanced the activity of the nickel catalysts.

A further increase in yield of 10 to 15 percent was obtained by carrying out the synthesis in several stages. It was found that by

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17/ Fischer, F., and Meyer, K., Brennstoff Chem. 14, 47, 64, 86 (1933).

18/ Fischer, F., and Pichler, H., Brennstoff Chem. 17, 24 (1936).

breaking up the synthesis into several steps and removing the products after each stage, the partial pressure of the carbon monoxide-hydrogen mixture, lowered by formation of reaction products, was restored, resulting in an increase in the yield of liquid and solid products.

B. Industrial Production of Catalyst

In 1934 the industrial development of normal-pressure synthesis was undertaken by the Ruhrchemie A.G. at Oberhausen-Holten. Particular credit for the technical development of the process on a large scale goes to F. Martin and L. Alberts.

Several changes in the composition of the cobalt catalyst were made at the Ruhrchemie. The amount of kieselguhr in the 100 Co: 18 ThO_2: 100 Kg catalyst was increased to 200 Kg, and magnesium oxide substituted for about half of the thorium oxide. Neither of these measures increased the laboratory yield of liquid and solid hydrocarbons, but the increased dilution of the cobalt offered advantages of a thermal nature, and the addition of magnesium oxide increased the mechanical strength of the catalyst.

The water used for the preparation of the catalyst must always be distilled. The cobalt should not contain more than 0.2 percent of calcium and 0.5 percent of copper. The presence of small amounts of nickel (about 0.2 percent) is desirable. When necessary, calcium is removed by precipitation with sodium fluoride. (For technical details, see report TOM Reel 19, Bag 3042, p. 41 and following). Industrial

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19/ Martin, F., Ind. Chemist, 13, 329 (1937).

kieselguhr, purified by thermal treatment, required no further purification. However, certain standards of quality were established. At first, the so-called "glühguhr" was used. Later, "röstguhr" which is treated at lower temperatures and is, therefore, somewhat less sintered and more active, was substituted. The calcium and iron content should be as low as possible.

Table 5. - Standards for Kieselguhr (Diatomaceous Earth)

	Glühguhr	Röstguhr
Preliminary thermal treatment, °C	1000	400-700
Density, g/l.	120-150	90-120
Sand content, Percent	<2	<2
Acid soluble (HNO_3) content, Percent		
Fe	1	1.7
Al	0.1	0.4
Ca	0.2	0.2
SO_4	0.4	0.6
Loss on calcination (1000°C.)	0.5	2.5

Reduction of the catalysts on a large scale is governed by the same considerations as in the laboratory. In order to avoid sintering, which would impair catalytic activity, reduction should take place at as low a temperature and as rapidly, as possible. The reduction process is facilitated by a rapid flow of hydrogen, containing as small an amount of oxygenated compounds as possible (exhaustive removal of water formed, short catalyst layers). Experience has shown that complete reduction is not desirable. In industrial synthesis apparatus, a hundred percent reduction gives too great an initial activity and shortens the life of the catalyst. Hence, for technical purposes, the degree of reduction was about 60 percent. The remaining oxide is useful in preventing further sintering. The reduction temperature, set at 360-365°C. for the 100 Co : 100 Kg catalyst, must be increased with the kieselguhr content. Thus, the 100 Co : 200 Kg catalyst requires a temperature of 390-395°C.

Reduction under these conditions requires special apparatus. Special precautions must be taken when charging the synthesis convertor with the reduced catalyst, to avoid oxidation reactions. This was achieved first at the KWI by saturating the catalyst with carbon dioxide, then in industry with paraffin, benzine, and Diesel oil, and later again with carbon dioxide. (In technical operation, surface of reduction batch, 1.5 square meters and catalyst bed of 35 centimeters. Rate of hydrogen flow, about 1000 cubic meters per square meter surface per hour. Reduction time, including preheating with hydrogen, about 1 hour. Cooling first with nitrogen, and below 100°C., with carbon dioxide. The reduction method in current use for technical purposes is in no way ideal. "Continuous" reduction would be far more desirable.) The carbon dioxide adsorbed on the catalyst surface prevents injury to the catalyst by air when it is charged to the synthesis converter and facilitates its conditioning. (For further details, see TOM Reel 19, Bag 3042, p. 41, etc.)

Experiments were also conducted at the Mülheim Institute for Coal Research to determine whether reduction temperatures could be lowered sufficiently so that reduction could be carried out directly in the synthesis apparatus. It was found that cobalt catalysts containing a few percent of copper, can be reduced at temperatures as low as 220°C. However, the life of the cobalt-copper catalysts was considerably shorter than that of catalysts containing no copper, probably due to progressive formation of cobalt-copper alloys. The undesirable effect of copper is much more marked with nickel than with cobalt. In consequence, the reduction of catalysts at low temperatures (in the converter) was abandoned.

C. Regeneration of Catalysts

From time to time, in normal pressure synthesis, it becomes necessary to remove by extraction the higher molecular weight products which accumulate on the catalyst and diminish its efficiency. This extraction is generally carried out with a higher boiling fraction of the synthesis products at a temperature somewhat below that used for the synthesis. It has also been suggested that extraction be replaced by treatment with hydrogen at the synthesis temperature. However, with this type of regeneration a portion of the catalyst paraffins is lost by decomposition to methane. Treatment with hydrogen after extraction is desirable, but not absolutely necessary. After about 6 or 8 months, the activity of the catalyst can no longer be restored sufficiently by extraction and treatment with hydrogen. The catalyst must then be removed from the converter, dissolved, purified if necessary, and reprecipitated.

A so-called hot regeneration, i.e., treatment with hydrogen at 400°C. has been suggested. Under these conditions hydrogen removes certain substances, such as carbon, which are not affected by the usual regeneration procedure and which interfere with the synthesis reaction. However, this method has found no application in industry, where the depleted catalyst is recovered by solution.

The life of the catalyst, or the period before regeneration or recovery of a catalyst becomes necessary, depends on the local conditions, on the kind of operation, and especially on the sulfur content of the synthesis gas.

D. Synthesis Gas

The synthesis gas used with cobalt catalysts is usually composed of 1 part of carbon monoxide and 2 parts of hydrogen. An increase in the carbon monoxide content of the synthesis gas results in increased olefin formation, but has an unfavorable effect in normal pressure synthesis on the life of the cobalt catalyst. Carbon dioxide, in presence of carbon monoxide and hydrogen (for instance, that which forms by the water gas shift reaction) behaves like an inert gas as long as any carbon monoxide is present. In the absence of carbon monoxide, it reacts with hydrogen to give methane

Water vapor is one of the chief reaction products of the synthesis with cobalt catalysts, and consequently is always present as one of the gases in the converter. Since at low temperatures, i.e., below 200°C., under the conditions of the synthesis, the rate of the water gas reaction -

$$CO + H_2O = CO_2 + H_2$$

is lower than that of the synthesis reaction, normally no appreciable amount of carbon dioxide forms in the presence of cobalt catalysts. Above 200°C. the amount of carbon monoxide conversion increases with the temperature. (Alkalised cobalt catalysts, and especially iron catalysts, favor carbon dioxide formation.) In the synthesis it is always well to keep the partial pressure of water low. (For experiments on syntheses in the aqueous phase, see F. Fischer and H. Pichler, Brennstoff. Chem. 20, 247 (1939).) The presence of nitrogen in the synthesis gas does no harm. However, in principle, it is desirable to keep the inert gas fraction as small as possible, first, because a decrease in the partial pressure of carbon monoxide and hydrogen has an unfavorable effect on the yield of higher hydrocarbons, and secondly,

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20/ Fischer, F., and Pichler, H., Brennstoff Chem. 14, 306 (1933).

because the passage of inert gases through the synthesis apparatus (especially when working at higher pressures) increases the cost of operation. The only advantage to be derived from diluting the synthesis gas with inert gases (particularly when active catalysts are used) is to control the heat of reaction. In the so-called "recycle" process, where fresh gas, mixed with the tail gas, is passed over the catalyst, this factor is of importance.

E. Gas Throughput

The gas throughput (liters of synthesis gas per hour per gram of cobalt) is determined by the activity of the catalyst, by the method of heat removal and lastly, by whether the maximum yield per volume of gas, or maximum space-time yields are desired. In Germany, where a particularly efficient utilization of the synthesis gas appeared desirable, the hourly throughput was 600 to 1000 liters per kilogram of cobalt (10-liter converter), the temperature being kept as constant as possible by use of narrow, water-cooled catalyst chambers. If the throughput of gas is increased, the yield per unit volume of gas decreases, but the space-time yields increase (see medium pressure synthesis with cobalt, fig. 4, and high-pressure synthesis with ruthenium, fig. 16).

F. Primary Reaction Products

The primary reaction products of the synthesis consist of paraffins and olefins, ranging from methane to high molecular weight solid paraffins. The boiling range of the products and the amount of unsaturated compounds present depend on the composition and age of the catalyst, on the composition of the synthesis gas, on the temperature, and other operating conditions. In 1935 Franz Fischer[21] gave the following average composition (Table 6) for the products (not including methane) obtained by synthesis in a single stage over 100 Co : 18 ThO_2 : 100 Kg catalyst at atmospheric pressure (CO : H_2 = 1 : 2).

Table 6. – Composition of Primary Reaction Products Obtained with 100Co: 18ThO_2 : 100 Kg Catalyst (Single Stage)

Constituent	Boiling range, °C.	Quantity, Weight Percent	Olefin content, Volume Percent
Gasol (C_3 + C_4)	below 30	4	50
Gasoline	30-200	62	30
Diesel Oil	above 200	23	10
Solid paraffins from oil	m.p. 50	7	—
Hard paraffins from catalyst	70-80 and over	4	—

According to F. Martin (Chem. Fabrik. 12, 233 (1939)), the following composition (Table 7) was found for the reaction products (including methane) obtained with a Co-ThO_2-MgO-Kg catalyst, in a two-stage commercial operation.

Additional values obtained during commercial operation in the presence of a 100Co : 5ThO_2 : 7.5MgO : 200 Kg catalyst are given in Table 8. Operation was carried out in two stages, with a throughput

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[21] Fischer, F., Brennstoff Chem. 16, 1 (1935).

Table 7. – Composition of Reaction Products Obtained with 100Co : 5ThO$_2$: 7.5MgO : 200Kg Catalyst (two stages)

Constituent	Weight Percent
Methane	18
Gasol (C_3 + C_4)	11
Liquid hydrocarbons boiling below 200°C.	43
Liquid hydrocarbons boiling between 200-300°C.	20
Paraffins	8

of 1 cubic meter of synthesis gas per kilogram of cobalt per hour in the first stage. The synthesis gas contained carbon monoxide and hydrogen in a ratio of 1 to 2, and 18 to 20 percent of inert components. The temperature was 180° to 195°C. For an 87 percent conversion of carbon monoxide, 148 grams of hydrocarbons having three or more carbon atoms was obtained. Four percent of the carbon monoxide was converted to carbon dioxide, 2.5 percent to C_2 hydrocarbons, and 12 percent to methane.

The Diesel oil showed an especially high ignitibility and consequently proved to be an excellent motor fuel. It can be used to raise the quality of lower-grade products. The anti-knock properties of the crude gasoline fraction do not fulfill the ordinary requirements. The quality of this gasoline can be improved in several ways. The gasoline can be treated by the usual procedure. It can also be mixed either with substances such as polymer gasoline (prepared from the unsaturated components of gasol), or with cracked gasoline. Lastly, its

Table 8 Values Typical of Normal Pressure Synthesis (100Co : 5ThO$_2$: 7.5MgO : 200Kg Catalyst)

Constituent	Weight percent of products listed	Specific gravity d_{15}	Olefins vol. per cent	S.K.Z.[1]	Average molecular weight	C-atoms in one molecule	Cloud Point	Pour Point	Octane number CFR research method	Cetane number HWA[2] motor	Cetene number
Gasol (C_3:C_4)	12	--	50	--	--	$C_3 + C_4$	--	--	--	--	--
Gasoline, to 185°C.	49.0	0.689	37	108	100	C_4-C_{10}	--	--	52	--	--
Gasoline, to 200°C.	54.5	0.693	34	115	115	C_4-C_{11}	--	--	49	--	--
Diesel oil, 185-320°C.	29.0	0.760	15	245	190	C_{11}-C_{18}	-13°	-18°	--	87	100
Diesel oil, 200-320°C.	24.5	0.756	13	260	205	C_{12}-C_{19}	-5°	-9°	--	92	105
Soft paraffins, 320-450°C.	7.0	0.900	Iodine number	--	--	$>C_{18}$	--	--	--	--	--
Hard paraffins, >450°C.	3.0	0.930	2	--	--		--	--	--	--	--

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[1] Boiling Point Index

[2] Heeres-Waffen Amt.

octane number can be raised by addition of lead tetraethyl. Under some circumstances, a combination of these various methods is advisable. The addition of 0.6 cubic centimeters of lead tetraethyl to 1 liter of primary gasoline boiling up to 170°C. raises the octane number from about 50 to 70; the addition of 1 cubic centimeter raises it from 50 to 73. If the gasoline is a lower-boiling cut, the octane numbers will be correspondingly higher.

G. Other Catalysts

Work with other catalysts, such as precipitated nickel catalysts, or combined precipitated cobalt-nickel catalysts (unpublished experiments at the KWI, Mülheim), did not give satisfactory results on a large scale. These catalysts tend to produce larger quantities of gaseous hydrocarbons. This is true to an even greater extent of nickel and cobalt skeleton catalysts (Raney principle). Although these catalysts are interesting from a scientific point of view, they were not economically practicable for large-scale use.

At the time of the development of the normal pressure synthesis iron catalysts produced only about half the yield obtained with precipitated cobalt catalysts, and had a life of only 4 to 6 weeks. It was not until the development of medium-pressure synthesis that iron catalysts achieved

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22/ Fischer, F., and Meyer, K., Brennstoff Chem. 12, 225 (1931). Brennstoff Chem. 14, 47, 64, 86 (1933).

23/ Fischer, F., and Meyer, K., Ber. Deut. chem. Gesell. 67, 253 (1934). Brennstoff Chem. 15, 84, 107 (1934).

importance. They will therefore be discussed at greater length under this heading. The most recent experiments with iron catalysts indicate their possible use in the synthesis at atmospheric pressure (see medium-pressure synthesis in the presence of iron catalysts, section "Synthesis at Medium or Normal Pressure").

2. Medium Pressure Synthesis with Cobalt

A. General Considerations

Soon after the discovery of normal pressure synthesis, experiments were undertaken at the Mülheim Institute for Coal Research to study the effect of pressure on the synthesis of hydrocarbons. The results of this series of experiments, covering the period from 1926 to 1933, were negative; it was observed that increased synthesis pressures offered no advantages, and only drawbacks.

Thus, according to Tropsch[24/]:

"The conclusion that pressure promotes the formation of higher hydrocarbons confirms our observations, which show that high-molecular weight paraffin hydrocarbons do indeed form at higher pressures; however, as was to be expected, they are retained by the catalyst. If the procedure is carried out at higher pressures in such a way that the reaction products separate from the catalyst, as in the case of operation at higher temperature, oxygenated compounds are formed, possibly as the result of a second order reaction."

Fischer and Pichler stated[25/]:

[24/] Tropsch, H., Brennstoff Chem. 8, 376 (1927).

[25/] Fischer, F., and Pichler, H., Brennstoff Chem. 12, 365 (1931).

"An increase in the pressure accompanying the catalytic hydrogenation of carbon monoxide favors the retention of high-molecular weight products by the catalyst. As a result, the catalyst is deactivated much more rapidly when operated under these conditions than at atmospheric pressure. At higher pressures, oxygenated compounds are obtained in place of hydrocarbons."

Fischer and Küster[26/] observed that:

"The effect of pressure again confirms the fact that, even when operating in liquid media, the hydrocarbon synthesis developed by F. Fischer and H. Tropsch is limited to operation at atmospheric pressure; in other words this synthesis is a completely independent reaction, which can only take place in the region of atmospheric pressure. As the pressure rises, the hydrocarbon synthesis tends more and more towards the formation of synthol, and instead of paraffin hydrocarbons, the formation of alcohols, fatty acids, etc., described elsewhere in connection with synthol occurs."

All these experiments were carried out with catalysts obtained by thermal decomposition. On the other hand, in 1936 F. Fischer and H. Pichler[27/] found that:

a. The use of precipitated cobalt-kieselguhr catalysts makes continuous operation possible even at higher pressure.

[26/] Fischer, F., and Küster, H., Brennstoff Chem. 14, 3 (1933).

[27/] Fischer, F., and Pichler, H., DRP 731, 295, August 2, 1936. Brennstoff Chem. 20, 41, 221 (1939). Ber. Deut. chem. Gesell. 72, 327 (1939).

b. The use of precipitated cobalt-kieselguhr catalysts in continuous operation does not result in conversion of the "hydrocarbon synthesis" into a "synthol" synthesis. Rather, it was found that, between these two regions, there exists a region of optimum pressure for the formation of higher-molecular weight paraffin hydrocarbons, which are continuously removed from the catalyst.

c. Whereas in "normal-pressure synthesis" the periodic decrease in conversion, for instance, every 4-6 weeks, necessitates regeneration of the catalyst, preferably by extraction, no such regeneration is required in the process which Fischer and Pichler have called "medium-pressure synthesis."

d. The total life of the catalyst is longer in medium-pressure synthesis than in normal-pressure synthesis.

e. The total yield of hydrocarbons containing more than 3 carbon atoms per molecule is higher in medium-pressure synthesis than in normal-pressure synthesis.

f. The increase in carbon monoxide-hydrogen conversion is not proportional to the increase in pressure with cobalt-kieselguhr catalysts. On the contrary, in order to obtain the same carbon monoxide conversion there must be an increase in contact time almost proportional to the increase in pressure. In other words, over the ranges of normal and medium-pressure synthesis, the amount of carbon monoxide and hydrogen converted by the cobalt catalyst per unit time is approximately independent of the pressure.

g. Other conditions being comparable, saturated hydrocarbons tend to form in larger quantities during medium pressure than during normal-pressure synthesis. (However, it is possible in medium-pressure synthesis to use carbon monoxide-rich synthesis gas without harm to the catalyst and thus to obtain larger amounts of olefins.)

In working at higher pressures, it was found necessary to dilute the concentration of the metal with kieselguhr. The higher the operating pressure, the more important this dilution was found to be. This fact was not observed in the earlier experiments which gave negative results.

In medium-pressure synthesis, it was found that the life of the catalysts was increased and that the need for periodic regeneration such as is necessary in normal-pressure synthesis, no longer existed. This can, in part, be explained by the fact that medium-pressure synthesis favors the formation of hydrocarbons which liquefy at the synthesis temperature and continuously wash the catalyst surface.

A characteristic difference between medium and normal-pressure synthesis, observed both in the laboratory and in industry, is the relative indifference of catalysts operated at medium pressures towards minor irregularities in the operating conditions. Constant maximum yields are more easily obtained at medium pressures. The fact that the formation of methane tends to be somewhat greater in normal pressure synthesis contributes toward making constant maximum conversion of carbon monoxide and hydrogen more difficult at normal than at medium pressures.

The following table gives comparative values for average production over one working month in a medium pressure and in a normal-pressure plant:

Table 9. - Comparison of Yields Obtained by Medium and Normal Pressure Synthesis

	Medium	Normal
$CO + H_2$ conversion, percent	92	87
Yield of liquid and solid hydrocarbons (in grams per standard cubic meter of synthesis gas)	145	125
$C_3 + C_4$, g/m^3	17	24
$C_1 + C_2$, g/m^3	21	26

The amount of product formed during any operating period (from the charging to removal of the catalyst) per ton of cobalt is about 50% higher in medium pressure than in normal-pressure synthesis (450 as against 300 tons of C_3+ product per ton of cobalt).

Another advantage, under the conditions prevailing in Germany, was the higher market value of the paraffins obtained. Operation at higher pressures involves additional expense in compressing the gases. Apparatus and operation also become more complicated at higher pressure. As a result, the experimental work has consistently been directed towards the development of catalysts that can be operated efficiently at lower pressures, preferably at atmospheric pressure.

B. Considerations on the Reaction Products

Figure 2 gives a graphic representation of the yields of paraffins, Diesel oil, and gasoline, obtained at a throughput of 1 liter of synthesis gas per hour per gram of cobalt, as a function of the pressure. The results represent the averages for 4 weeks of operation (single stage, no recycle, no regeneration), using a 100Co : 18ThO_2 : 100 kieselguhr catalyst. The curves show the region of maximum paraffin formation and the maximum total yield. They also demonstrate that the size of the Diesel oil fraction formed remains approximately constant over a considerable range. The upper limit of the operating pressure is determined by the beginning of carbonyl formation, resulting in a more rapid decrease of catalytic activity.

Table 10 (similar to Table 8 for normal pressure of synthesis) gives the average composition and properties of the products obtained in

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28/ Fischer, F., and Pichler, H., Brennstoff Chem. 20, 41 (1939).

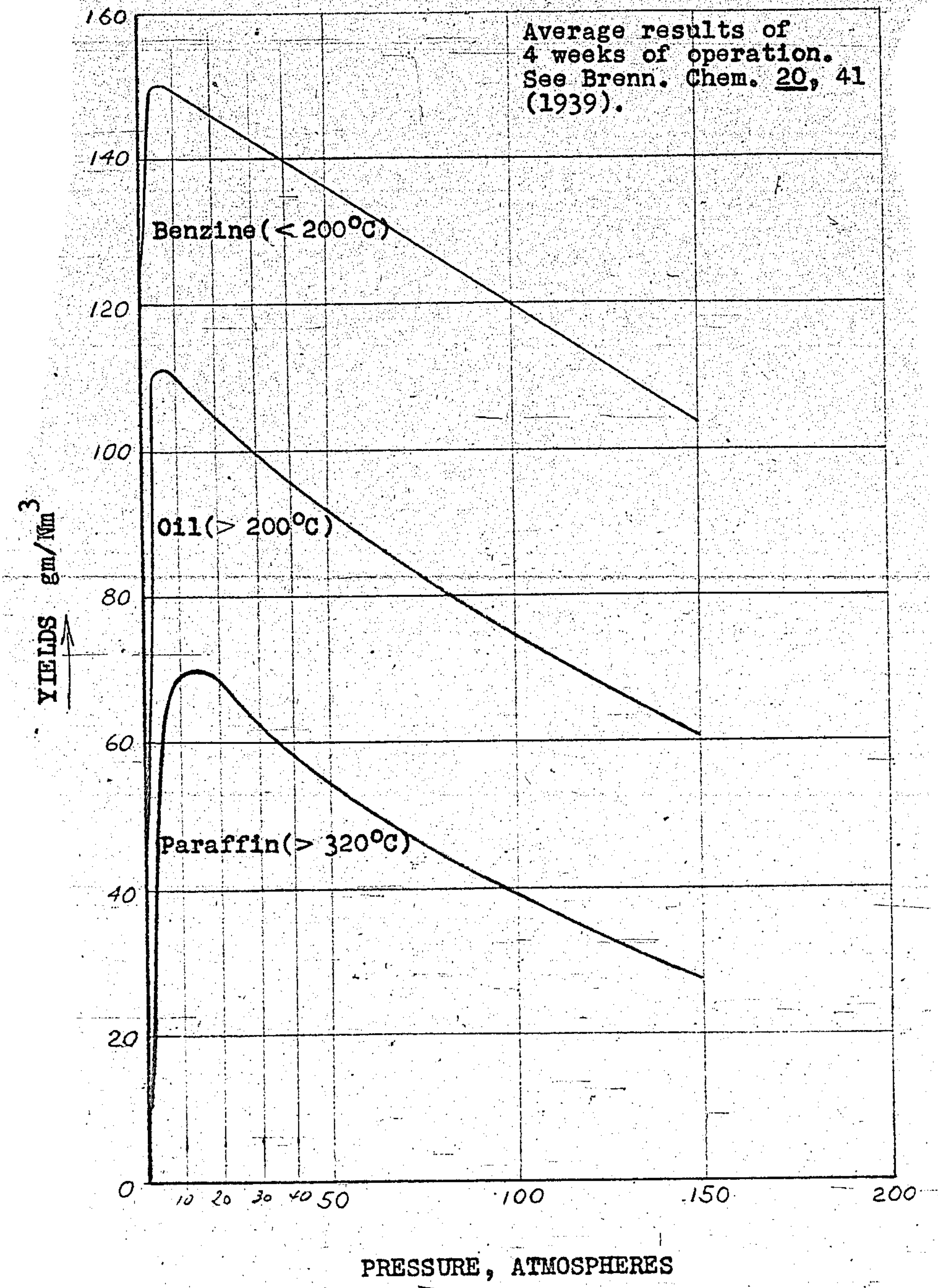

Figure 2: Cobalt middle-pressure synthesis. Relation of yields to pressure.

commercial medium-pressure synthesis with cobalt (standard operating procedure, no recycle, and 100Co : 5ThO_2 : 7.5MgO : 200 Kg catalyst). This type of procedure favors the direct formation of high molecular-weight paraffins and Diesel oil. If directly marketable gasoline is desired as a product, the primary gasoline can be mixed with gasoline obtained by cracking of the higher fractions.

Table 10. - Typical Values for Results Obtained by Medium-Pressure Synthesis

Press: 7 atm. abs.
Temp.: 175-195°C.

Throughput: 1/m^3 synthesis gas/kg. Co/hr.
Synthesis Gas Composition: CO : H$_2$ = 1 : 2; 18-20% inert components
Standard procedure (no recycle)

Constituent	Weight percent of total products listed1/	Specific gravity d_{15}	Olefins vol. per-cent	S.K.Z.2/	Average molecular weight	C-atoms per molecule	Cloud Point	Pour Point	Octane number CFR research method	Cotane number	Cete numb
Gasol(C_3+C_4)	--	--	30	--	--	66% C_4 33% C_3	--	--	--	--	--
Gasoline, to 185°C.	35	0.685	20	110	100	C_4-C_{10}	--	--	26	--	--
Gasoline, to 200°C.	40	0.689	18	120	115	C_4-C_{11}	--	--	25	--	--
Diesel oil, 185-320°C.	35	0.760	10	240	190	C_{11}-C_{18}	+7	-11	--	87	100
Diesel oil, 200-330°C.	35	0.766	8	255	205	C_{11}-C_{19}	-2	-5	--	92	10
Soft paraffins, >320°	30	0.90	Iodine number 2	--	--	>C_{18}	--	ca.80	--	--	--
>330°C.	25	0.90		--	--	>C_{19}	--	ca.80	--	--	--

1/ Yield: 145 grams of liq. products/Nm^3 + 10 grams of gasol.
2/ Boiling point index.

C. Maximum Yields of Solid Paraffin and Diesel Oil

As was to be expected from their high degree of saturation, the solid paraffins and Diesel oil obtained by medium-pressure synthesis with cobalt are of exceptionally high quality. Although by varying pressure, temperature, extent of conversion, and catalyst, it is possible to vary the solid paraffin content of the reaction product considerably, the amount of primary Diesel oil cannot be controlled in this way. Comparison of the products obtained with a 100 Co : 18 ThO_2 : 100 Kg catalyst and a 100 Co : 5 ThO : 7.5 MgO : 200 Kg catalyst showed that the catalyst which contains less kieselguhr and no magnesium favors paraffin formation. The Diesel oil fractions, on the other hand, showed no appreciable difference. Experiments with catalysts containing a higher cobalt content (Co:Kg$>$1) gave liquid and solid products containing 50 to 55 percent of solid paraffin and 25 percent of Diesel oil. The solid paraffin fraction may possibly be increased still further by adding manganese to cobalt catalysts. Using a cobalt-manganese catalyst, Rölen (Ruhrchemie) obtained liquid and solid products containing 64 percent of solid paraffins at the exceptionally low reaction temperature of 165 to 168°C. and 10 atmospheres. Thorium also favors the formation of high boiling products. Similarly, the addition of alkali promotes the formation of higher

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29/ Fischer, F., and Koch, H., Brennstoff Chem., vol. 13, 61, 1932.

molecular weight products. However, owing to their shorter life, alkalized cobalt catalysts have found no place in industry to date.

In general, increasing the pressure (limit is 20 to 30 atmospheres because of carbonyl formation), lowering the temperature and the gas throughput all increase the solid paraffin yield. Thin catalyst layers give higher solid paraffin yields than are obtained with deep beds. Finally, the amount of solid paraffin present in the products decreases as the catalyst becomes older, with a corresponding rise in the amount of lower molecular weight hydrocarbons formed.

In the light of current research, a satisfactory procedure for the production of Diesel oil should involve careful thermal cracking of the primary solid paraffins (eventually with subsequent or simultaneous hydrogenation). Under certain conditions, it would be possible to obtain 60 percent of the product in the form of Diesel oil.

D. Synthesis of Olefins

The olefin content of the synthesis products may be increased by operating with a carbon monoxide-rich gas. Water gas ($CO : H_2 = 1 : 1$) is known to promote olefin formation in normal-pressure synthesis; but it is generally avoided owing to its deleterious effect on the catalyst under these operating conditions. It can, however, be employed in medium-pressure synthesis. With water gas composed of carbon monoxide and hydrogen in the ratio of 1 : 1.2 the gasoline fraction obtained from the synthesis contains 40 percent of olefins, instead of the 20 percent formed with mixed gas ($H_2 : CO = 2 : 1$), and the Diesel oil fraction contains 20 to 25 percent of olefins instead of 10 percent.

By raising the carbon monoxide content of the synthesis gas, the amount of olefins can be increased still further. Thus, a gas that contains hydrogen and carbon monoxide in a ratio of 1 : 2 produces a gasoline with almost 70 percent of olefins. At the Ruhrchemie such a gas was obtained by recycling over the catalyst at a pressure of 7 atmospheres gauge a mixture of 1 part of fresh water gas to 2 to 3 parts of recycle gas until a ratio in the end gas of $1H_2$:2CO was produced. With a hydrogen-carbon monoxide ratio of 0.767 : 1, in the in-gas, a gasoline (<200°C.) fraction with 61 percent of olefins and a Diesel-oil fraction with 45 percent of olefins are obtained. Table 11 compares the results from such an experiment (2) with an experiment using water gas with no recycle (1).

It should be noted that, in order to use as much of the carbon monoxide as possible, the end gas from the recycle operation must in general be adjusted by the addition of hydrogen to a composition of $2H_2$+1CO and then converted by a second-stage operation of the synthesis in a single pass. The total result then corresponds to a combined recycle and normal operation.

Table 11. - Effect of Recycling on the Medium-Pressure Cobalt Synthesis (Example Taken from a Patent Application by the Ruhrchemie)

	(1)	(2)
Type of gas	Water gas	Water gas
Type of operation	Single pass	Recycle, 1+3
Gas throughput, N m^3/hr.	37.2	37.2 (converter inlet, 148.8)
Temperature, °C.	192	202
Pressure, atmospheres absolute	7	7
Ratio H_2:CO in water gas	1.28:1	1.28:1

Table 11. – (Cont'd.)

Percent $CO+H_2$ conversion	60.3	62.7
Fresh gas		
Percent CO	38.2	38.2
Percent H_2	48.7	48.2
In gas		
Percent CO	38.2	41.7
Percent H_2	48.7	32
End gas		
Percent CO	41.8	
Percent H_2	27.9	
Ratio H_2:CO in converter in-gas	1.28:1	0.767:1
Olefins, volume percent		
In gasoline, boiling to 200°C.	39	61
In Diesel oil, 200 to 300°C.	23	43

As will be seen from figure 3, the increase in olefin production depends neither on the recycle process, nor on the increased rate at which the gas circulates due to recycling, but is determined only by the ratio of carbon monoxide to hydrogen of the synthesis gas entering the converter. The points K are based on recycling experiments at different temperatures and gas throughputs (where 1 + 3 = 1 part of fresh gas + 3 parts of recycle gas), chosen at random. The points gD are based on single pass experiments (standard procedure). The curve gives the olefin content as a function of the H_2-CO ratio. The products of the process with and without recycling lie on the same curve. Recycling simply constitutes a convenient method of bringing a carbon

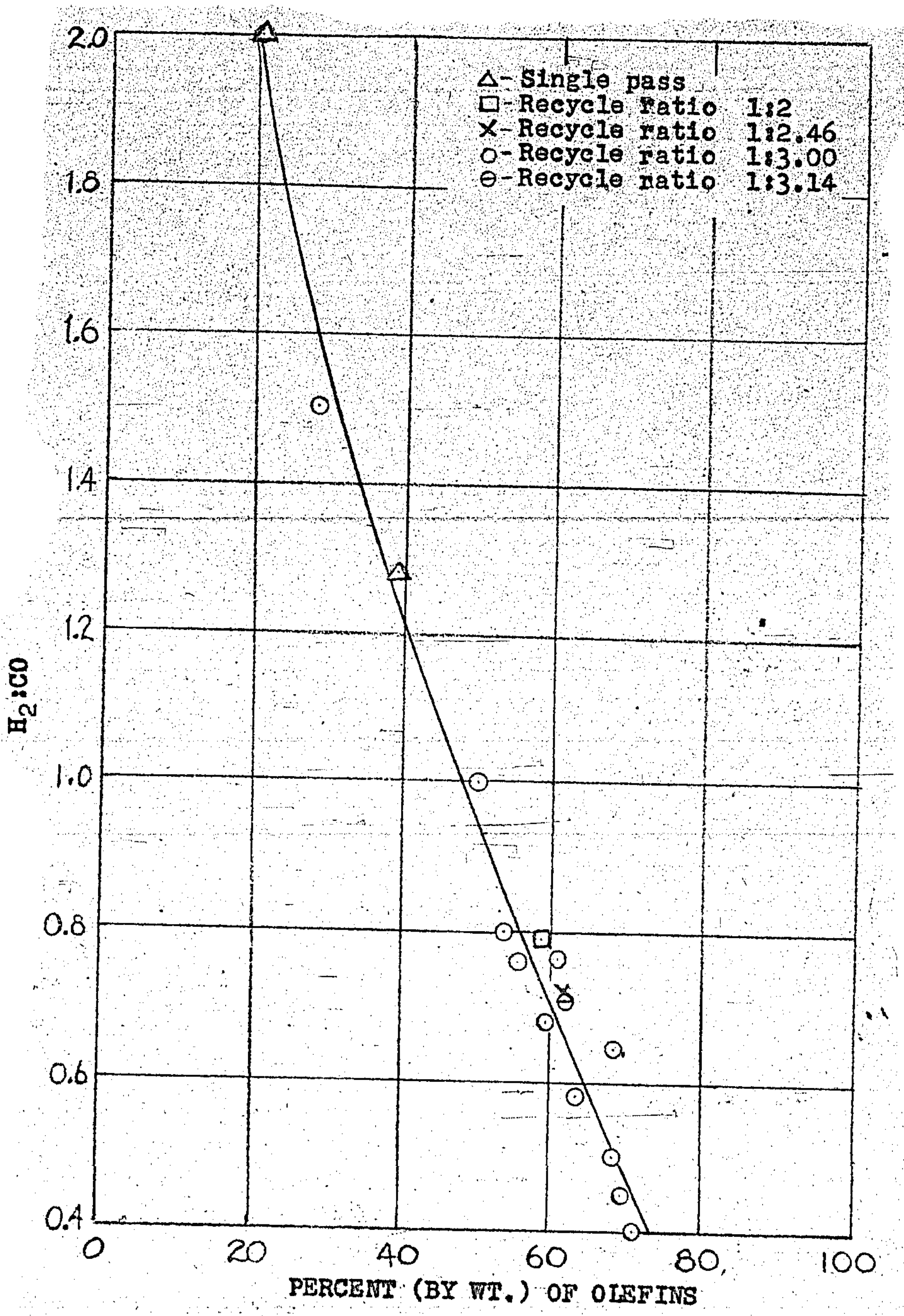

Figure 3: Influence of the H_2:CO ratio on the olefin content of the Benzine(< 200°C)

monoxide-rich synthesis gas in contact with the catalyst. It also contributes to the uniformity of the operations and, consequently, to an increase in the life of the catalyst.

In addition to improving the knock rating of the gasoline fraction, increased olefin production was of value for later use in the OXO Synthesis (see medium pressure synthesis, iron catalysts) and in the synthesis of lubricating oils.

For the production of lubricating oils by the polymerization of olefins in the presence of aluminum chloride, the olefins from the medium pressure cobalt synthesis are more suitable than those from iron catalysts, because the latter contain relatively large amounts of oxygenated compounds.

E. Discussion of Yields Based on the Unit Volume of Synthesis Gas and on the Unit Volume of Catalyst (Space-Time Yields)

These considerations on medium-pressure synthesis in the presence of cobalt catalysts are concluded with a discussion of yields. Operation was carried out in two stages, in water cooled tubes having a diameter of 10 millimeters and in the presence of a fixed catalyst (100 Co : 18 ThO_2: 100 Kg). The synthesis gas contained carbon monoxide and hydrogen in a ratio of 1 to 2. The synthesis pressure was 10 atmospheres. Figure 4 shows conversion as a function of gas throughput. Gas throughputs (liters per gram cobalt per hour) are shown on the

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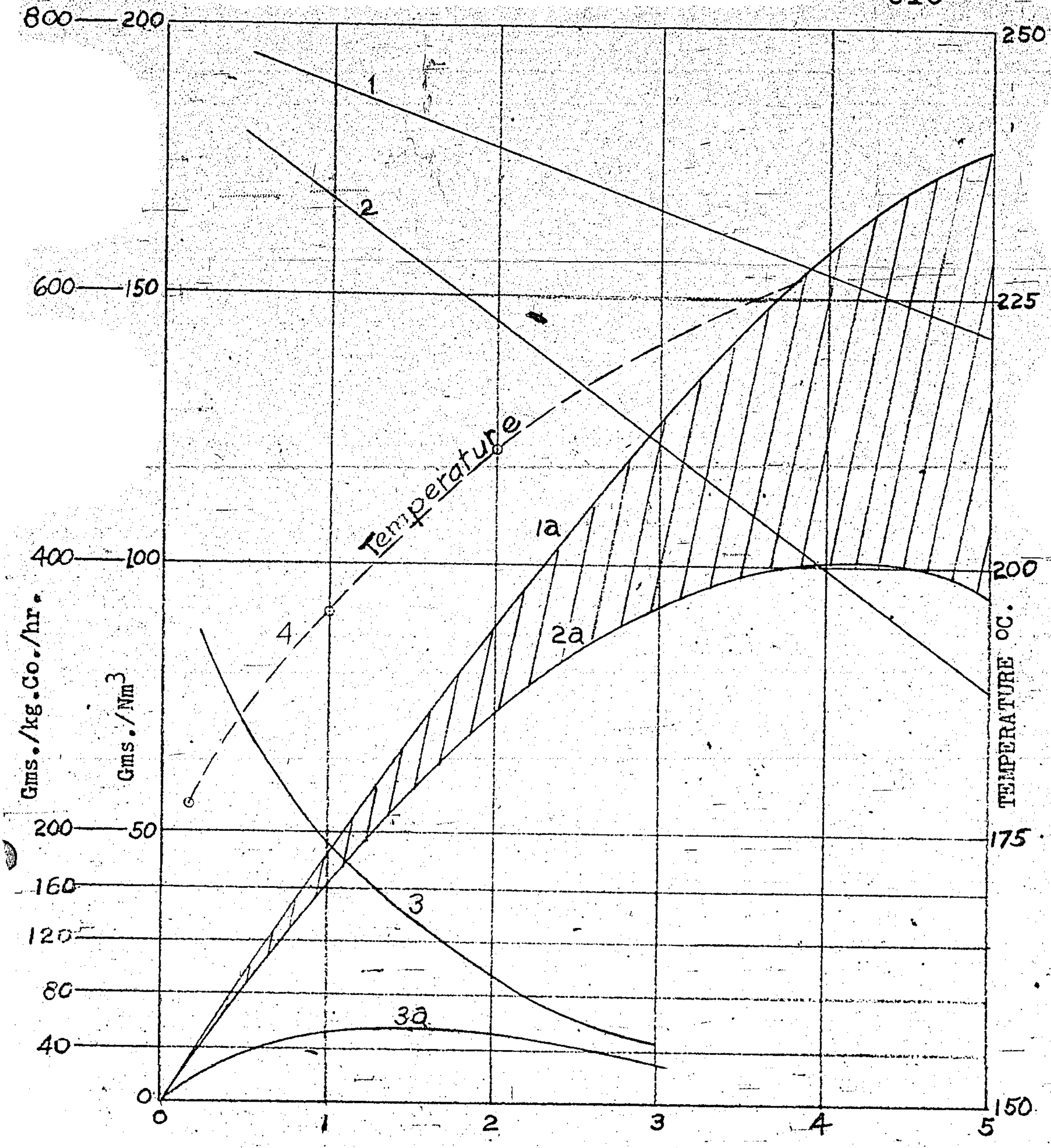
30/ Fischer, F., Koch, H., and collaborators, Brennstoff Chem., vol. 14, 463, 1933; vol. 15, 229, 1934; vol. 16, 261, 1935; vol. 19, 327, 1938; vol. 20, 413, 1939; vol. 21, 169, 1940; vol. 23, 67, 1942.



THRUPUT in L/gm.Co/hr.

Figure 4: Cobalt middle-pressure synthesis. Influence of gas thruput on yields.

abscissa and the yields (grams per normal cubic meter of synthesis gas and grams per kilogram of cobalt per hour) (10 liters catalyst volume) on the left ordinates and the synthesis temperatures corresponding to the different throughputs, the right ordinate. Curves 1, 2, and 3 are based on yields per unit volume of throughput gas; curves 1a, 2a, and 3a are the corresponding curves for the yields per kilogram of cobalt, and curve 4 gives the rise in temperature required by an increase in throughput. Curves 1 and 1a give the total yields, including methane, curves 2 and 2a give the yields in hydrocarbons with more than 2 carbon atoms per molecule, curves 3a give the yields of paraffins that are solid at room temperature. The regions between curves 1 and 2, and 1a and 2a therefore represent methane formation.

For a throughput of 1 liter of synthesis gas per gram of cobalt per hour, yields consisted of 168 grams of higher hydrocarbons (C_3 and over) and 22 grams of methane per normal cubic meter of ($CO+H_2$) (11.6% CH_4): in other words, 168 grams of higher hydrocarbons per kilogram of cobalt per hour.

When the gas throughput is increased, two possible limiting procedures present themselves. In the first case, the $CO - H_2$ conversion may be maintained by a corresponding rise in temperature (associated with a rapid rise in methane formation). If the temperature is kept constant, a corresponding decrease in gas conversion occurs. In the experiments shown in figure 4, an intermediate path was chosen. As the gas throughput was increased, the temperature was raised, but only sufficiently to maintain a maximum yield of higher hydrocarbons

(C_3 and above); in other words, the increase in gas throughput is inevitably accompanied by a decrease in gas conversion.

For a throughput of 2 liters of synthesis gas per gram of cobalt per hour, yields of 145 grams of higher hydrocarbons and 33 grams of methane (18.5%) per normal cubic meter ($CO+H_2$) were obtained. This corresponds to 290 grams of higher hydrocarbons and 66 grams of methane per kilogram of cobalt per hour.

For a throughput of 4 liters of synthesis gas per gram of cobalt per hour, yields of 100 grams of higher hydrocarbons and 55 grams of methane (35.5%) per normal cubic meter of ($CO+H_2$) were obtained. This corresponds to 400 grams of higher hydrocarbons and 220 grams of methane per kilogram of cobalt per hour.

If the gas throughput is increased still further, there is a drop not only in the yields per unit volume of gas, but also in those per unit volume of catalyst (space-time yield).

Paralleling the increase in gas throughput from 1, to 2, and then to 4 liters of synthesis gas per hour, an increase in temperature from 195° to 210°C., and then to 227° was necessary. Such an increase in temperature has a harmful effect on the life of the catalyst. In the third experiment, i.e., at 227°C., it would mean that the operation starts at the temperature which ordinarily would not be reached until about a year later. Moreover, with the conventional type of middle pressure converter currently used in industry (annulus with 10 millimeter catalyst layer), operation with 4 liters of synthesis gas per hour is precluded, owing to the problem of removing the heat of reaction. Under these conditions, operation at high temperatures would lead to the formation of methane and carbon.

In Germany, the need for full utilization of gas and energy made it necessary to operate under such conditions that maximum yields of higher hydrocarbons were obtained per unit volume of throughput gas. As will be seen from figure 4, the yields per unit time and volume could be increased considerably by changing operating conditions. It is true that, together with a corresponding reduction in gas costs (or in energy costs for multiple conversion), increased throughput results in decreased efficiency of heat removal and therefore shorter catalyst life and increased amounts of the lower-boiling fraction (see figure 4, paraffin curves 3 and 3a).

3. Medium Pressure Synthesis in the Presence of Iron

(In connection with the present paper, the reader is referred to the report by H. Pichler, "Report on the Middle-Pressure Synthesis with Iron Catalysts," prepared in June 1940, at the KWI for Coal Research, Mülheim/Ruhr. This report will be found in Reel 101, Doc. PG-21559-NID and has been translated by M. Lewa, Bureau of Mines, Pittsburgh, Pa. It is available in the report, "Translations of German Documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis. Part I (Second Edition)". An abstract of this report was given by H. Pichler, Sept. 9, 1940, in connection with a series of lectures at the Mülheim Institute. The text of this lecture will be found in Reel 101, Doc. PG-21574-NID and has been translated by M. Lewa. It is available in the same report of translations. A more detailed report by H. Pichler and H. Merkel, entitled, "Chemical and Magneto-Chemical Study of Iron Catalysts", is being prepared, which discusses the problem of carbide and carbon formation during pretreatment of iron catalysts and the subsequent synthesis.)

A. General Considerations

In contrast to the extensive development of the cobalt synthesis, none of the work undertaken at different times, from 1927 to 1936, in connection with normal pressure synthesis in the presence of iron catalysts, gave results of any practical interest. Neither the introduction of precipitated catalysts, nor the dispersion of the catalyst on kieselguhr, which produced excellent results with the cobalt and nickel synthesis, gave comparable results when applied to iron catalysts. The life of the iron catalysts extended from 4 to 6 weeks and the average yields of liquid hydrocarbons amounted to 50 or 60 grams per cubic meter of synthesis gas. The decisive step in iron catalyst synthesis was made in the winter of 1936-1937 (F. Fischer and H. Pichler) when a precipitated iron catalyst that had been in use at atmospheric pressure for several weeks, was switched to operation at a synthesis-gas pressure of 15 atmospheres. The yields were almost doubled, and the life of the catalyst was increased several fold.

In order to utilize existing equipment, attempts were made to prepare iron catalysts whose activity at temperatures below 250°C. would be comparable to that of the cobalt catalysts. Systematic research showed that iron catalysts should undergo a preliminary treatment at a low pressure, for instance, atmospheric pressure, with a carbon monoxide-containing gas such as water gas. An iron catalyst pretreated at atmospheric pressure produced a carbon monoxide conversion during synthesis at 240°C, which could not be reached below 290°C, with a catalyst put directly into the synthesis at 15 atmospheres. Moreover, the yields of higher hydrocarbons were better at lower temperatures. Attempts made at that time to reduce the catalysts with hydrogen were not successful. The optimum pressure for the synthesis of hydrocarbons in the presence of iron catalysts lies between 10 and 20 atmospheres.

Subsequent work on iron catalysts was governed largely by the desire to develop iron catalysts with a maximum activity at the lowest possible temperatures, so that, should iron come to replace cobalt in the industrial process, the same synthesis equipment could be retained. This equipment, in which the heat of reaction was removed by boiling water under pressure, was so constructed that pressure on the water side could not exceed about 25 atmospheres, corresponding to a maximum synthesis temperature of 225°C. Where no limits are imposed by the design of the apparatus, the synthesis may be carried out at higher temperatures and with a high conversion of carbon monoxide. However, it should be noted that as the temperature of the reaction rises, the composition of the products shifts towards the more volatile hydrocarbons.

Lower reaction temperatures can be used with hydrogen-rich than carbon monoxide-rich synthesis gases. Instead of carbon dioxide, large amounts of water are formed. The liquid reaction products are completely colorless, and the solid hydrocarbons are just as white as those obtained with cobalt catalysts. However, the amount of oxygenated products is larger than with carbon monoxide-rich gases. Figure 5 gives the relation of the optimum synthesis temperature to the gas composition for a given catalyst and a space velocity of 200 (volumes of gas per volume of catalyst space per hour). The increase in the H_2:CO ratio from 1:1-to-4:1 makes a possible decrease of 40° in the reaction temperature. Simultaneously however, the amount of carbon monoxide available for conversion drops in the proportion of 2.5:1.

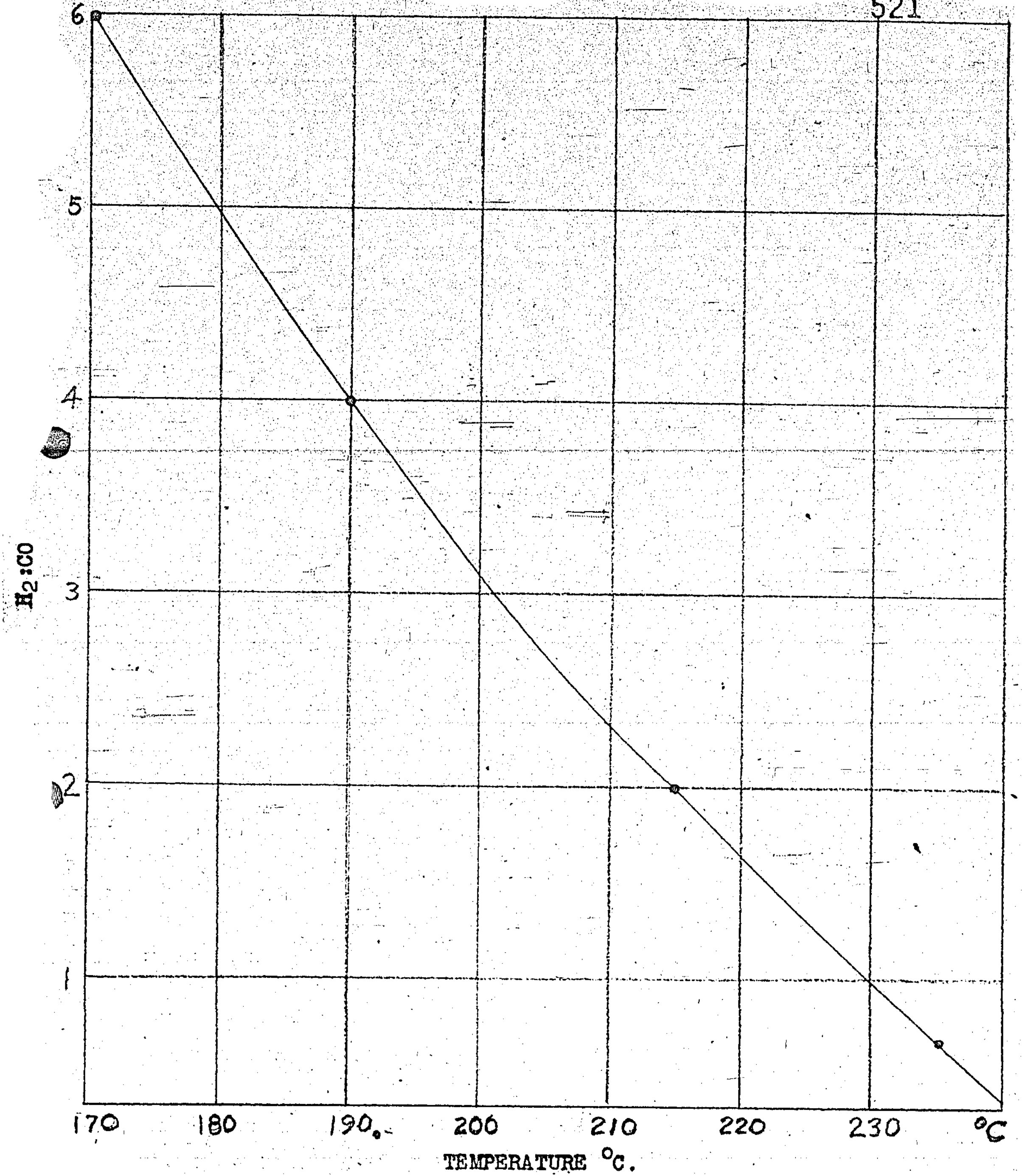


Figure 5: Relation between synthesis gas composition and optimum synthesis temperature.

The increase in the hydrogen content of the gas has a favorable effect on the life of the catalyst in that it decreases the tendency towards carbon formation and promotes a continuous "activation" of the catalyst surface.

The composition of the synthesis gas and the reaction temperature, as well as the synthesis gas pressure and the space velocity, each influence the course of the overall reactions given by the following equations,

$$1.\quad 2CO + H_2 = CH_2 + CO_2$$

$$2.\quad CO + 2H_2 = CH_2 + H_2O$$

in such a way that reaction 1, initially the course over iron catalyst, is progressively repressed in favor of reaction 2 as the hydrogen content, pressure, and space velocity increase and the temperature of the reaction decreases. It is believed that equation 2 is the fundamental equation of the synthesis for iron and cobalt; however, in the presence of iron catalysts, a secondary reaction, the water-gas shift,

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

takes place. This latter reaction can be inhibited, or retarded, by the changes in operating conditions, as suggested above.

B. Preparation and Composition of Iron Catalysts

In the case of cobalt catalysts, a standard catalyst, except for minor variations, the precipitated $Co-ThO_2-Kg$ catalyst, gave the best results in the hydrogenation of carbon monoxide. Iron catalysts, on the other hand, may be prepared in a number of different ways, according to the operating conditions and the synthesis products required. Essentially they can be divided into the following groups:

precipitated catalysts;
thermally decomposed and sintered catalysts;
fused catalysts.

Precipitated catalysts are used when highly active iron catalysts, giving good yields of hydrocarbons at a low temperature, are desired. These catalysts are usually prepared from a dilute solution of the salt by precipitation with a solution of sodium carbonate. Ferric solutions ordinarily give hard glossy catalysts that have a conchoidal fracture; ferrous solutions give less compact catalysts of an earthy consistency. Experiments at the KWI showed that ferrous-ferric mixtures are particularly satisfactory. The method of preparation is similar to that used for cobalt catalysts (see Schwarzheide experiments). Granules of different sizes (including pelleted catalysts)were prepared for use in fixed beds.

At the Mülheim Institute for Coal Research, iron catalysts were subjected to a conditioning treatment with a carbon monoxide-containing gas such as water gas. Highly active iron catalysts, containing little (1%) or no copper were obtained by pretreatment with carbon monoxide at 1/10 atmosphere and 325°C. With catalysts containing more copper (10 to 20%) best results were obtained by pretreatment with synthesis gas at 220 to 240°C. and atmospheric pressure. The carbides that form during treatment with carbon monoxide give the catalyst an active structure that promotes the formation of higher hydrocarbons. Reduction of the iron catalyst with hydrogen was suggested (see Part V). However, iron catalysts developed at the Mülheim Institute gave better results when first treated with a gas containing carbon monoxide. In general, the lower the temperature at which the synthesis is to be carried out, the more important the preliminary treatment becomes. At a synthesis temperature of 300°C. satisfactory conversion is obtained even without special preliminary treatment.

Decomposition catalysts may be used when it is not essential that the synthesis be carried out at the lowest possible temperature. These catalysts have a slightly lower activity than those prepared by precipitation. However, their preparation is considerably simpler.

Iron nitrate, or some other easily decomposed iron salt mixed with the appropriate promoters, is thermally decomposed at the lowest possible temperature. The catalyst is obtained as a powder. When organic substances, such as starch, are added before decomposition a voluminous powder is obtained. If the catalyst is to be used in a fixed bed, the powder can be compressed into pellets. Catalysts in finely powdered form are suitable for liquid-phase suspension units. Catalysts prepared by thermal decomposition of iron carbonyl are also suitable for this purpose (prepared for instance by passing iron carbonyl, diluted with inert or reducing gases, into hot oil). Preliminary treatment similar to that described for precipitated catalysts is desirable for the decomposition catalysts which are obtained as oxides. Experiments conducted at the KWI with decomposition catalysts at 15 atmospheres and 240° gave satisfactory conversion after the catalysts had been subjected to preliminary treatment with synthesis gas ($CO : H_2 = 3:2$) at atmospheric pressure and 250°. By increasing the temperature 2 to 3° each week, conversion could be kept constant over half a year. (German patent application St. 56856, November 23, 1937.) Sintered iron catalysts are used under special conditions, such as the hot gas recycle process. Their superior ability to conduct heat, as compared with that of finely divided catalysts, is emphasized. As raw material for the preparation of such catalysts iron powder prepared by decomposition of iron carbonyl is used. As in the case of other iron catalysts, some alkali is added to retard the formation of gaseous hydrocarbons. In practice, the iron powder is moistened with a dilute alkali solution (such as 1% of potassium as potassium borate, based on iron), and is then extruded into little granules which are sintered in a current of hydrogen for four hours at 850°C. The catalyst has a density of more than 7, and a bulk density of about 2.5.

Fused catalysts of the synthetic ammonia catalyst type may also be used for the hydrocarbon synthesis. In this case iron is fused with various promoters in a current of oxygen and carefully reduced (see Schwarzheide experiments I.G.).

According to the I.G., optimum conditions for reduction prescribe passage of hydrogen over the catalyst at a space velocity per hour for 48 hours of 3000. (This type of reduction would enormously increase the cost of the otherwise inexpensive preparation.)

As the synthesis proceeds, the catalyst, originally present as reduced iron (x-ray studies at I.G. -Merseburg show that the iron oxide is converted entirely to α-iron), is converted progressively to the Fe_2C carbide (hexagonal).

A characteristic difference between fused and precipitated catalysts is that the former produces smaller middle fractions (Diesel oil) in favor of the lighter and heavier fractions.

In some ways the fused catalysts are reminiscent of the skeleton catalysts prepared by Franz Fischer and Karl Meyer[31]. In the latter case, the lattice rearrangement, necessary for catalytic activity, is obtained by removing aluminum, or silicon, whereas in the case of fused catalysts this rearrangement is brought about by "extracting" the oxygen during reduction. In connection with the fused catalysts developed by the I. G. Farbenindustrie, the Russian patent discussed by Troitskii[32] should be mentioned. According to this patent, fused catalysts not only of iron, but also of nickel and cobalt, are suitable as hydrogenation catalysts.

It was found at the Mülheim Institute that iron catalysts possessing a high degree of activity could be prepared without the addition of promoters. However, in general, the addition of promoters is desirable as a means of controlling the type of products obtained.

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[31] Fischer, F., and Meyer, K., Brennstoff Chem., vol. 15, 84, 107, 1934.
Raney, Jour. Am. Chem. Soc., vol. 54, 4116, 1932.

[32] Troitzkii, Oel und Kohle, vol. 36, 73, 1940. Russian patent 54,392, 1939.

The alkali content of the iron catalyst is particularly important as will be seen from table 12. The amounts of alkali indicated represent weight percent of potassium carbonate based on metallic iron. Where other alkali salts (for example, permanganate, fluoride, etc.) are indicated, the notation "1% $KMnO_4$" means the amount equivalent to 1% of K_2CO_3.

The table shows the nature and quantity of the products formed in the presence of various alkalized catalysts during operation at 235°C. and 15 atmospheres with a synthesis gas composed of 3 parts of carbon monoxide and 2 parts of hydrogen. During the first month, the yields in grams per normal cubic meter of ideal gas fluctuated between 140 and 160 grams, indicating that contraction was not constant. It was apparent that the addition of alkali did not affect the activity of the catalyst, but only the distribution of products. The yields obtained over a long period of time with a catalyst prepared by precipitation with ammonia and containing no alkali were not significantly lower than those from an iron catalyst containing 1/4 percent of K_2CO_3. On the other hand, the alkali content plays an important part in determining the type of products obtained. In the absence of alkali, the solid paraffin fraction, determined by the butanone method and based on the total yield of solid, liquid, and gasol hydrocarbons, amounted to 12 percent. Addition of 1/4, 1, 2, and 5 percent of potassium carbonate, respectively, increased the yields obtained to 26, 42, 43, and 45-46 percent. As the alkali content increases, a corresponding decrease is observed in the amounts of liquid and gasol hydrocarbons produced.

Table 12. – Yields Obtained from Iron Catalysts Containing Different Amounts of Alkali. (Single Stage1/)

Precipitant	Alkali Addition Percent	Solid, Liquid, Gasol Hydrocarb. Grams/Nm^3 of Ideal gas	Paraffins Percent	Liq. Hydro-Carbons Percent	Gasol Percent
NH_3	0	141	12	67	21
Na_2CO_3	0	141	13	67	20
–	0.25 K_2CO_3	148	26	56	18
Na_2CO_3	1 K_2CO_3	157	42	47	11
"	1 $KMnO_4$	155	41	45	14
"	1 K_2SiO_3	158	43	41	16
"	1 K_2F_2	163	46	42	12
"	1 K_2HPO_4	154	38	52	10
Na_2CO_3	2 K_2CO_3	143	43	44	13
"	5 "	161	45	43	12
"	5 "	155	46	44	10

1/ Table 6, H. Pichler, lecture, Mülheim/Ruhr, Sept. 10, 1940 (Reel 101, Doc. 21574-NID).

Table 12 also shows that during the first weeks of operation the amount and type of products are not influenced by the nature of the potassium salt added to the catalyst. Experiments with 1 percent of potassium carbonate and those using equivalent amounts of potassium permanganate, silicate, fluoride, and phosphate, all gave the same results, within the limits of experimental error. Increasing the alkali content promoted the formation of oxygenated products. As regards the ratio in which hydrogen and carbon monoxide are consumed, the decreasing tendency of alkalized catalysts to hydrogenate the primary products to saturated hydrocarbons results in an increase in carbon monoxide consumption and a decrease in that of hydrogen. The life of catalysts is longer for a low alkali content, such as 1/4 percent of potassium carbonate, than for a high one.

Alkali is usually added to the catalyst as follows. After precipitation with sodium carbonate, the catalyst is washed until it is free of alkali. It is then made up into a slurry and a calculated amount of alkali added with stirring. The liquid is removed by evaporation and the catalyst dried. Direct precipitation with potassium carbonate or hydroxide and washing to the desired alkali content have also been suggested. Precipitation with a sodium compound has the advantage of being less expensive.

Addition of copper may have an important effect on the behavior of iron catalysts. Just as in the case of cobalt, the addition of copper lowers the reduction temperature for iron. However, the effect of copper on the life of the iron catalyst is not as adverse as on cobalt. Experiments by Fichler and Merkel (unpublished) show that an iron catalyst containing 1 percent of copper reached the same degree of carburization after 1/2 hour that was attained in 12 hours by a copper-free catalyst. After 5 hours, the copper-containing catalyst consisted chiefly of iron carbide, with only very small amounts of oxide, whereas the copper-free catalyst was still composed essentially of Fe_3O_4. Experiments conducted at the I.G. show that the presence of copper also has a stabilizing effect on the unstable hexagonal Fe_2C (see Part V).

Addition of copper in small amounts has a favorable effect on the reducibility, the carburization, and the reproducibility of the more active iron catalysts (that is, on those that operate at lower temperatures).

The preparation of iron catalysts containing 20 percent and more of copper has been suggested. Experiments at the KWI indicate that such high copper contents would be of interest only for synthesis at low temperatures in the normal pressure synthesis. Large amounts of copper also promote the formation of higher boiling compounds. High temperatures, whether during pretreatment or operation, have a harmful effect on the life of iron catalysts with a high copper content.

The addition of kieselguhr resulted in sharp improvement in the life and activity of cobalt and nickel catalysts. This is not true of iron catalysts. Whereas the high hydrogenating power of cobalt, and especially of nickel, necessitates "dilution" with kieselguhr of the catalytic metal present per unit volume, the less active iron catalysts give the same conversion to higher hydrocarbons, whether kieselguhr is added or not. Under similar conditions, catalysts containing kieselguhr have a greater tendency to promote the formation of lower boiling products, than do catalysts with no kieselguhr. Nevertheless, in industry, when the apparatus provides inadequate heat removal, it is sometimes expedient to use iron catalysts containing kieselguhr in order to prevent undesirable carbon formation. The presence of a limited amount of kieselguhr makes the freshly precipitated iron catalyst more filterable.

Of the other possible carriers, silicic acid is thought to increase mechanically the strength of the catalyst (see experiments at Schwarzheide, Lurgi). Aluminum oxide is known to increase the activity of nickel catalysts and the thermal stability of their crystal lattice, in the same way as does thorium oxide. Addition of aluminum oxide in small amounts (3 to 4 percent) to precipitated catalysts increases their tendency to form alcohols. Addition of larger amounts increases the ability of the catalyst, particularly above 300°, to split off water from alcohols formed during synthesis. The use of calcium and magnesium oxides has been suggested for similar reasons. In the ammonia synthesis, it was observed that addition of aluminum, calcium, and potassium oxides in small amounts decreased the energy of activation of iron catalysts (I.G.). Cerium, vanadium, and similar metals are said to favor the formation of oxygenated products (Ruhrchemie). Traces of arsenic in fused catalysts are believed to give higher yields of esters (acids). The effect of addition of promoters such as aluminum and calcium oxides is not the same for all iron catalysts. In general, variations in amounts of promoters (or even omission of promoters) can be compensated for by varying the operating conditions, in order to achieve the same results.

The possibility of regenerating iron catalysts by extraction with solvents or by treatment with hydrogen is similar to that discussed for cobalt catalysts. In general, this type of "reactivation" is necessary only in the normal pressure synthesis, particularly when the synthesis is operated under conditions that promote the formation of higher hydrocarbons.

C. Reaction Conditions and the Catalyst

The activity of the iron catalyst is to a great extent dependent upon the operating temperature. If the temperature is too high, carbon and methane form; if it is too low, the conversion of carbon monoxide and hydrogen is poor. For optimum conversion, the choice of the catalyst should depend upon the conditions under which the synthesis is to be operated. At lower reaction temperatures very active catalysts are necessary. The higher the synthesis temperature, the simpler, less expensive, and less active the iron catalysts that can be used.

Where high yields of solid paraffins are required, the operating temperature must be kept low. If low-boiling gasoline hydrocarbons are to be the main product, operation at higher temperatures is indicated. High space-time yields are achieved at high temperatures, whereas the best yields per unit volume of gas (for a single pass of gas over the catalyst) are obtained at low temperatures. The diagram in figure 6 shows the relation that exists between the reaction temperature and the catalyst.

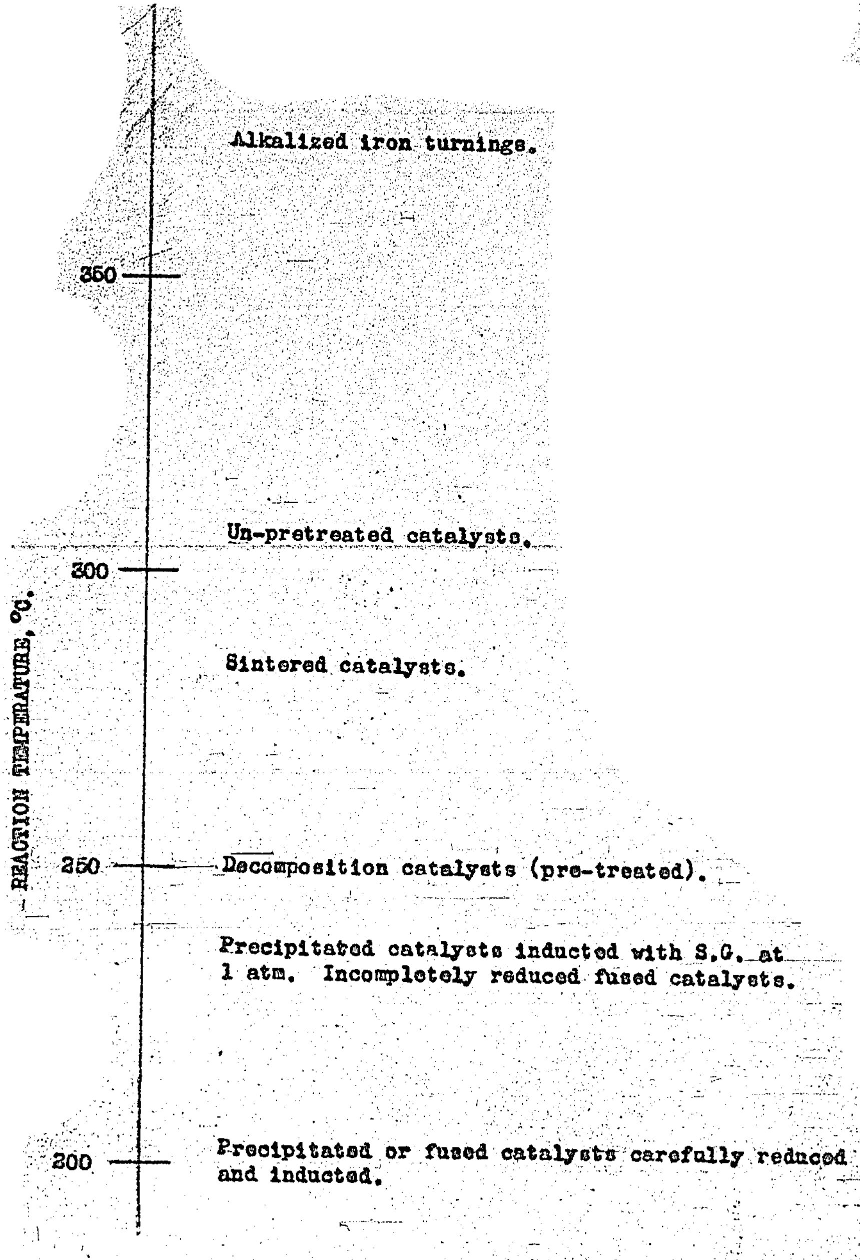

Figure 6: Proper reaction temperatures for various catalysts.

Below 220°, operation is possible only with iron catalysts prepared by special methods. Precipitated catalysts, pretreated at low pressure (high space velocity of gas) with carbon monoxide or a mixture of carbon monoxide and hydrogen, were used for this purpose at the KWI. At the I.G. suitable catalysts were prepared by careful reduction (over a period of several days) of fused catalysts with hydrogen at a high space velocity. In the region of 230°C., precipitated catalysts can be used that have been pretreated with synthesis gas at atmospheric pressure and are present in an incompletely reduced (or carburized) state. The reduction of fused catalysts also requires less care than that required for operation in the region from 200 to 220°C. At 250°C., decomposition catalysts, pretreated at atmospheric pressure with synthesis gas, were used with success at the KWI (iron catalysts pretreated for use at 220°C. would give too large an amount of carbon at this temperature).

At still higher temperatures, sintered decomposition catalysts may be used. For an initial operating temperature of 300°, unpretreated precipitated and decomposition catalysts give good conversion. If the temperature is increased still further (an increase in pressure is necessary to retard formation of volatile products) a region is reached between 380 and 400°, where Fischer and Tropsch were able to carry out their Synthol synthesis simply with alkalized iron filings. At 450°, catalytic conversion of carbon monoxide and hydrogen to higher hydrocarbons will take place even in an empty iron tube (although accompanied by large amounts of carbon and methane).

Naturally, no sharp limit exists between the individual catalyst types and their range of application. Thus, depending upon the nature of the promoters present and the method of pretreatment, fused and precipitated catalysts with varying degrees of activity may be prepared. Moreover, in order to maintain the rate of conversion, the reaction temperature must be raised progressively for all catalysts to compensate for their gradual decrease in activity during synthesis. The temperatures given in figure 6 represent the initial temperatures. Finally, for a given catalyst, an interdependence exists between the gas throughput and the optimum reaction temperature at which optimum conversion is obtained. Figure 7 shows this relationship for a precipitated catalyst, pretreated at atmospheric pressure. Synthesis temperatures are plotted on the abscissa, optimum throughputs of synthesis gas on the ordinate. In the region of the curve shown in the figure optimum conditions prevail. With higher temperatures and a low gas throughput, a region is reached where carbon and methane form abundantly, whereas increased throughput and lower temperatures result in incomplete conversion of carbon monoxide and hydrogen.

Numerous other operating conditions must be considered when choosing a suitable iron catalyst. For instance, for high throughputs over a fixed catalyst bed (hot gas recycle) the catalyst granules must have great mechanical strength. The granule strength of the standard precipitated cobalt catalyst was sufficient for the technical-scale process generally used in Germany; but it would not have been satisfactory for the hot gas recycle process.

When a fluidized catalyst bed is used, the best suspensions are

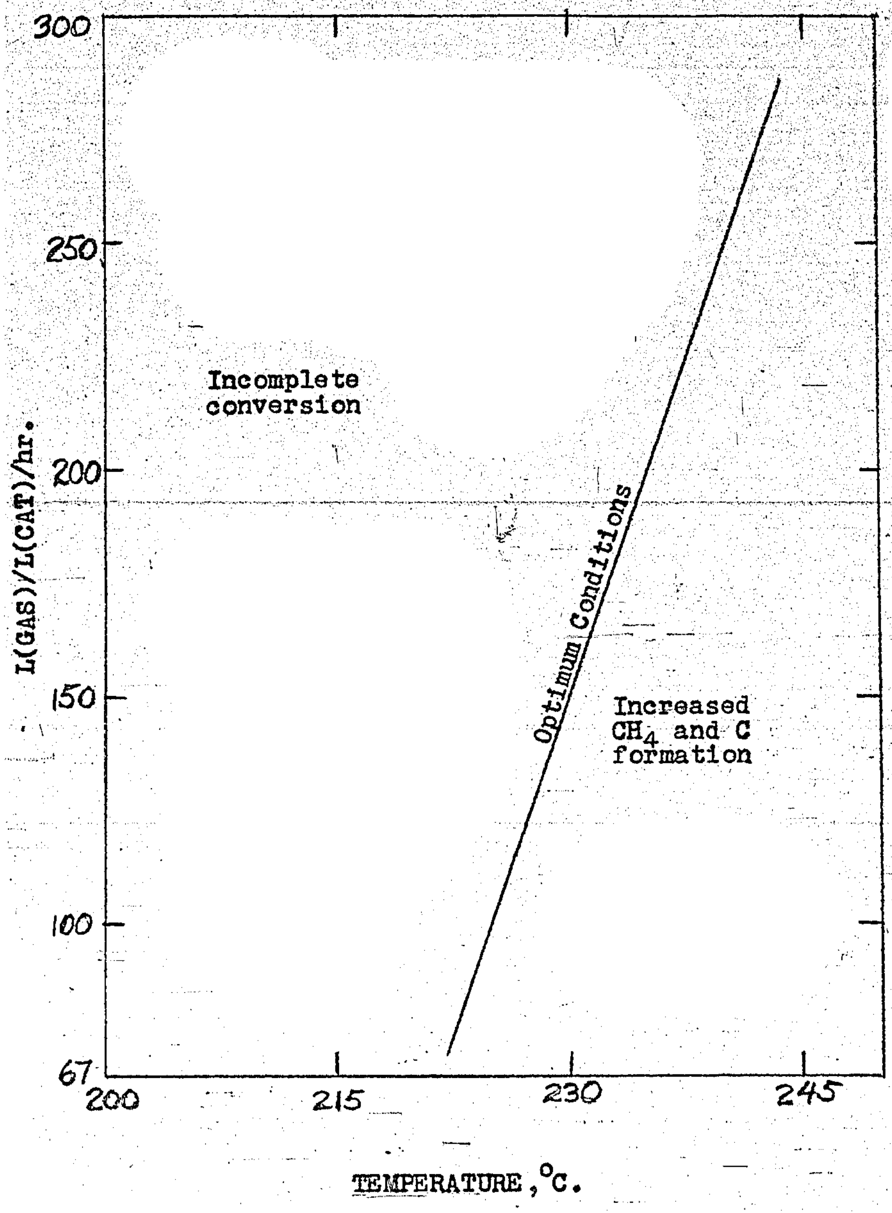

Figure 7: Relation between gas thruput and synthesis temperature with pre-treated precipitated catalysts at 1 atm.

obtained with very finely divided dry catalysts. In this case, precautions must be taken to prevent damage to the apparatus by the abrasive action of the catalyst granules and to avoid changes in the catalytic activity as a result of decomposition of the catalyst.

D. Single Stage Synthesis with Carbon Monoxide-Rich Synthesis Gas

Over the temperature range of 230 to 250°C., carbon monoxide and hydrogen are converted in a single pass (without recycling), in a ratio of 3:2. If maximum yields are to be obtained for a single pass of the gas over the catalyst, the synthesis gas employed must contain carbon monoxide and hydrogen in the ratio in which they are used, as described in the experiments given in Table 12. Analysis of the outlet gas given in Table 13 shows that operating conditions for iron catalysts may be maintained constant for considerable periods with a synthesis gas of this type. In this instance, a copper-free iron catalyst containing 1/4 percent of potassium carbonate was operated at a gas pressure of 15 atmospheres.

These experiments were carried out in reaction tubes (standard laboratory aluminum block furnace), inclined in such a way that the catalyst did not fill the entire cross section of the tube. Above the catalyst was a very minute empty space, so that the gas that passed over the catalyst encountered little resistance.

Table 13. – Analyses of Outlet Gas from an Experiment with an Iron Catalyst Pretreated with Carbon Monoxide at 255° and 1/10 Atmosphere (Operation at Space Velocity of 200)

Months Operated	Temp. °C.	Contraction %	CO_2 %	Unsaturates %	O_2 %	CO %	H_2 %	Hydrocarbon %	C_2	N_2 %
1	253	50	49.6	2.2	0.1	15.0	13.3	8.8	1.9	11.0
14	254	50	50.1	2.8	0.2	14.9	11.9	7.3	1.7	12.8

Analyses of Outlet Gas from an Experiment with an Iron Catalyst Pretreated with Carbon Monoxide at 325° and 1/10 Atmospheres (Operation at Space Velocity of 200)

Months Operated	Temp. °C.	Contraction %	CO_2 %	Unsaturates %	O_2 %	CO %	H_2 %	Hydrocarbon %	C_2	N_2 %
1	235	54	57.0	2.6	0.1	5.3	14.6	8.9	2.0	10.5
3-1/2	235	52	51.2	3.3	0.1	5.2	11.2	9.0	1.9	10.0

When these same experiments were carried out with a fixed catalyst bed in vertical tubes, the use of carbon monoxide-rich gas resulted in a progressive pressure drop over the catalyst, due to the formation of small quantities of free carbon. In consequence, synthesis apparatus must be used in which a slight expansion of the catalyst does not matter (on the subject of fixed catalyst beds, see F. Fischer and H. Pichler[33/]) as, for instance in the liquid phase; another alternative

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33/ Fischer, F., and Pichler, H., Patent DRP 708,500.

is to use carbon monoxide-poor gas with recycling or in two steps with intermediate regeneration of synthesis gas from the gaseous products formed in the first step. Catalysts that contain copper and little alkali are less apt to form carbon than catalysts having a high alkali content and no copper. In addition, the tendency to form carbon decreases at lower reaction temperature. In the "Schwarzheide experiments", for instance, no appreciable increase in pressure drop over the catalyst was observed after operating with standard water gas in vertical reaction tubes over a period of three months. The same is true of the experiments described under the heading "Synthesis in the Presence of Iron Catalysts at Medium or Normal Pressure", where vertical layers of fixed catalyst bed were used without any preceptible formation of carbon.

E. Comparative Experiments at Schwarzheide

In December 1937, and again in September 1940, Franz Fischer, and H. Pichler conferred with representatives of the industries interested in the synthesis of hydrocarbons, in the lecture room of the Mülheim Institute, and reported on the essential details concerning synthesis conditions for iron catalysts. Since substitution of cobalt by iron was highly desired, experiments (TOM Reel 37, Bag 3451/22d and 24) with iron catalysts in medium-pressure synthesis were undertaken both by the research laboratories of both the licensees of Fischer-Tropsch synthesis process and some affiliated industrial enterprises. Details of the results obtained were not make known immediately. When, at the beginning of 1943, it became apparent that a cobalt shortage would soon make itself felt in Germany, a series of comparative experiments for the purpose of studying experimental developments obtained by different groups, seemed indicated.

Experimental Conditions

In the eventuality of cobalt being replaced by iron, it appeared eminently desirable to reduce the reconversion of the industrial equipment involved to a minimum. Consequently, from the first, specific directives were laid down for the comparative experiments, and the workers required to abide by them. These rules were as follows:

a. Standard water gas is to be used as synthesis gas.

b. The synthesis temperature must not exceed 225°C.

c. The synthesis gas pressure is 10 atmospheres.

d. The experimental runs are to be scheduled for three months, with no reactivation during this period.

e. Owing to the demands of the market, the synthesis products must correspond as closely as possible to those obtained with cobalt catalysts, hydrocarbons with two or more carbons, and later with three or more carbons, being uniformly priced.

f. The immediate object was to obtain maximum yields in a single stage, with a single pass of the gas.

The synthesis apparatus in all experiments consisted of water-cooled double tubes, 4.5 meters long and containing approximately 4.8 liters of catalyst. The thickness of the catalyst layer between the double tubes was 10 millimeters. The dimensions of the apparatus corresponded throughout with those existing in medium pressure converters used in industry.

Participation in the experimental work was as follows:

1. Kaiser Wilhelm Institut für Kohlenforschung, Mülheim-Ruhr (KWI) (Converter 1).
2. Lurgi, Gesellschaft für Wärmetechnik m.b.H., Frankfurt-Main (L) (Converter 2).
3. Braunkohlenbenzin A.G. Werk Schwarzheide (BB) (Converter 3).
4. I.G. Farbenindustrie A.G. Ludwigshafen (IG) (Converter 4).
5. Ruhrchemie A.G. Oberhausen-Holten (RCh) (Converter 5)
6. Treibstoffwerk Rheinpreussen, Homberg-Niederrhein (RhPr) (Converter 6).

The actual experiments were carried out at the Braunkholenbenzin A.G. at Schwarzheide under the supervision of representatives of the 6 participants.

Catalysts Used

The exact composition and the details of preparation of the catalysts used were not made public at first. At the conference at Göttingen, September 5, 1944, after termination of the experiments, the following data (Table 14) were published.

Table 14. - Catalyst Composition (Based on a 10-Cubic Meter Converter)

	Iron Metric Tons	Copper (Zinc) Kg.	Alkali Content Percent	Carrier	Pretreatment (Reduction)
KWI	6	60	0.75 K_2CO_3 (based on Fe)	None	Water gas
L	3.9	390	30% potassium silicate (based on Fe, 9% K_2O)	Silicic acid (potassium silicate)	Hydrogen (30% reduction)
BB	6.9	690 (690)	0.5 K_2CO_3 (based on Fe)	None	Water gas 245° (synthesis gas)
I.G.	18.0	-	1% K_2CO_3 (based on catalyst)	Al_2O_3 CaO (up to 2%)	Hydrogen 500°
RCh	2.5	125	0.5 to 2% K_2CO_3 (based on Fe)	Kieselguhr	Hydrogen
RhPr	2.7	135	0.5 to 1% K_2CO_3 (based on Fe)	Pulverized impure dolomite	Hydrogen 300 to 400° and water gas 245°

The experiments were run as planned for 90 days, under the prescribed operating conditions. After operating for a few days, the KWI substituted a catalyst containing 3/4 percent of potassium carbonate for the original one containing 1/4 percent of potassium carbonate, in order to obtain higher boiling products. BB and RhPr were obliged to recharge their converters with fresh catalyst several times in the beginning, owing to mechanical difficulties. Two days before the close of the 90-day experimental period, the KWI converter suffered a breakdown because of a drop in the level of the cooling water.

The results of the tests at Schwarzheide may be summarized as follows:

Converter 1 (KWI)

The catalyst, 100 Fe-1Cu-0.75 K_2CO_3, was precipitated from a warm nitrate solution (60-70°) containing ferrous and ferric ions in a ratio of approximately 1 : 1 and 1 percent copper by a boiling solution of sodium carbonate. After precipitation, the slurry was heated briefly to 100°C., filtered, and washed free of alkali. The catalyst was then reslurried in water and an aqueous solution of potassium carbonate (0.75 percent, based on iron) was carefully added with stirring. The mixture was evaporated to a paste on the water bath, and dried at 110°C. for 24 hours. The dry catalyst was crushed to granules of 2-4 millimeters in size and pretreated with water gas at 325° and 1/10 of an atmosphere (4 liters at 1 atmosphere per 10 grams of iron per hour).

Converter 2 (L)

The only information given regarding the catalyst used here will be found in Table 14. As a rule, the Lurgi catalysts contained aluminum oxide, in addition to copper and potassium silicate. TOM Reel 37, Bag 3451/24 gives the following example of composition and method of preparation:

$$100\ Fe\text{-}5\ to\ 10\ Cu\text{-}9\ Al_2O_3\text{-}9K_2O\text{-}24\ SiO_2.$$

The boiling solution of the nitrates of iron, copper, and aluminum was poured into boiling potassium hydroxide solution (more recently a solution of sodium carbonate was used) until a pH value of 9 was reached. The precipitate was washed and centrifuged. The prescribed amount of potassium silicate was incorporated into the washed catalyst. The catalyst was reduced with hydrogen (1 cubic meter per liter of catalyst per hour, about 40 minutes) at 250 to 300°C. Reduction should produce a metallic iron content of 25 to 30 percent as rapidly as possible.

Converter 3(BB)

The catalyst composition was 100 Fe - 10 Cu - 10 Zn - 0.5 K_2CO_3. The catalyst was very probably precipitated with a solution of sodium carbonate and then alkalized with potassium carbonate in much the same way as the KWI catalyst. Pretreatment was carried out as usual for catalysts with a high copper content, with water gas at atmospheric pressure and about 230°.

Converter 4 (IG)

The catalyst was prepared by fusing a mixture of 100 Fe 2 (Al_2O_3 + CaO), and 1 K_2CO_3 in a current of oxygen. The fusion temperature was about 1500°. Careful reduction is of particular importance in the case of fused catalysts. In general, reduction is carried out with a space velocity of hydrogen of 400-3000 for 48 to 72 hours, at 450-500°C. This procedure removes all oxygen. The iron is present in the catalyst as α iron. According to the IG, fused catalysts tend to agglomerate during synthesis. As compared with precipitated catalysts, the cost of preparation is lower, that of reduction higher.

Converter 5 (RCh)

The composition was first given as : 100 Fe - 5 Cu - 50 kieselguhr - 0.5 to 2 percent of K_2CO_3. Later information given by Dr. Roelen[34] during his interrogation in London, indicated that the catalyst also contained 10 percent CeO_2, based on iron. As a rule, the Ruhrchemie catalysts contain not cerium, but calcium oxide (10 percent CaO, based on iron). The RCh catalysts were prepared by precipitation in the early days with potassium hydroxide, and later with a solution of sodium carbonate. Before being put into the synthesis with water gas, the catalysts were reduced with hydrogen for about 24 hours at 300°.

The following procedure for the preparation of a catalyst of this type was given by the Ruhrchemie in 1944:

Iron catalyst of composition 100 Fe - 5 Cu - 10 CaO - 30 Kg.

Solution of 6400 grams of sodium carbonate in 50.4 liters of water.

Solution of 1.8 kilograms of iron and the calculated amounts of copper and calcium, as the nitrates, in 50.4 liters of water.

The boiling iron solution is poured slowly into the boiling carbonate solution, stirring constantly until no further carbon dioxide is evolved.

540 grams of kieselguhr are added.

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[34] Hall, C. C., Craxford, S. R., Gall, D., Interrogation of Dr. Otto Roelen of Ruhrchemie, A.G., BIOS Final Report No. 447, Item 30, 1946, p. 23.

The slurry is heated to boiling briefly, filtered, and washed with 100 liters of water.

The moist cake is kneaded with 3 percent potassium hydroxide (based on iron; 100 grams of potassium hydroxide per liter).

The cake is dried at 105° and granulated as usual, then reduced for 1 hour at 300° with 300 liters of hydrogen per 50 cubic centimeters of catalyst.

Converter 6 (RhPr)

The catalyst composition was 100 Fe - 5 Cu - 0.5 to 1.0 K_2CO_3 on dolomite (containing 91% $CaCO_3$?) as carrier. It was prepared by precipitation and reduced at atmospheric pressure, first with hydrogen at 300 - 400°C. and then with water gas at 245°C.

Experimental Results

The rules a, b, c, d, and f, prescribed earlier (p. 61) were followed for all the experiments.

Table 15 gives the gas throughput (normal cubic meters per 10 cubic meters of catalyst per hour) for the 6 experimental converters, calculated for a 10-cubic meter converter (standard unit). The average conversion of ($CO+H_2$) and of carbon monoxide, the synthesis temperature at the end of the experiment, the average total yield (including C_1,C_2, and oxygen) in grams per normal cubic meter of synthesis gas (88% $CO+H_2$), and the yield in tons per day calculated for a 10-cubic meter converter, are also shown.

Table 15. - Results of Schwarzheide Experiments (Single Stage)

	KWI	Lurgi	B.B.	I.G.	R.Ch.	Rh.Pr.
Gas throughput, Nm^3/ hr/ 10 m^3 converter	1087.5	1069	1107	1150	1038	1040
CO + H_2 conversion, Percent	68.3	64.8	58.2	65.1	54.2	57.2
CO conversion, %	85.0	87.8	77.0	81.0	70.0	62.0
End temperature, °C.	224	220	225	220	222	224
Total yield, g/Nm^3 synthesis gas	125.2	124.4	108.3	117.1	103.1	104.0
Total space-time yields, (tons per 10 m^3 converter space per day)	3.27	3.19	2.88	3.23	2.57	2.60
Paraffin fractions, tons/day						
paraffins	0.573	0.788	0.992	0.545	0.559	0.301
olefins	0.007	0.142	0.138	0.085	0.051	0.009
alcohols & esters	0.010	0.190	0.110	0.050	0.050	0.030
Diesel oil fraction, tons/day						
paraffins	0.373	0.126	0.148	0.136	0.162	0.273
Olefins	0.067	0.165	0.222	0.164	0.078	0.067
Alcohols & esters	0.020	0.130	0.100	0.060	0.090	0.010
Gasoline fraction, tons/day						
Paraffins	0.383	0.202	0.131	0.261	0.228	0.369
Olefins	0.392	0.318	0.339	0.489	0.252	0.371
Alcohols & esters	0.040	0.100	0.040	0.070	0.090	0.030
C_3 + C_4 hydrocarbons, tons/day						
paraffins	0.310	0.131	0.068	0.175	0.140	0.260
olefins	0.340	0.259	0.232	0.425	0.230	0.300
C_1 + C_2 hydrocarbons, tons/day	0.545	0.350	0.240	0.540	0.350	0.440
Lower alcohols	0.200	0.290	0.120	0.230	0.290	0.140

The products were divided into fractions: paraffin fraction (molecules with more than 18 carbon atoms), Diesel oil fraction ($C_{11} - C_{18}$), gasoline fraction ($C_5 - C_{10}$), also ($C_3 + C_4$) hydrocarbons, ($C_1 + C_2$) hydrocarbons, and lower (water-soluble) alcohols. The individual fractions were subdivided into saturated and unsaturated hydrocarbons, and oxygenated organic compounds.

The synthesis gas used contained 12 percent of inert components. Carbon monoxide and hydrogen were present in the ratio of 1:1.25. In order to obtain a good space-time yield in tons per day, the gas throughput for all experiments was somewhat higher than is usual in industry with cobalt catalysts. For the purpose of obtaining high yields in a single stage, as prescribed, operations were carried out with the highest possible carbon monoxide conversion. The degree of conversion was limited by the maximum temperature allowed, which was set at 225°.

The ratio in which carbon monoxide and hydrogen were converted by the different catalysts, differed. It was 0.80 for converter 1; 0.66 for converter 2; 0.69 for converter 3; 0.74 for converter 4; 0.72 for converter 5, and 1.07 for converter 6.

It is interesting to note that at approximately the same temperatures iron catalysts of widely differing compositions gave very similar space-time yields. Thus converter 1 gave 3.27; converter 2 gave 3.19; and converter 4, 3.23 tons per day of primary products. The catalysts used in converters 1 and 2 were precipitated catalysts, containing 1 and 10 percent of copper respectively.

On the other hand, catalyst 4 contained small amounts of aluminum and calcium oxides, but was prepared as a fused catalyst, similar to the synthetic ammonia catalysts. The Ruhrchemie catalyst was the only one to have kieselguhr as carrier (50 percent, based on iron). The iron density, for example, the amount of iron present per unit volume of catalyst, also varies considerably, ranging from 2.5 to 18 tons per 10-cubic meter converter. Finally, it is probable that the degree of reduction varied considerably from catalyst to catalyst. Lurgi limited reduction to 30 percent, whereas the I.G. catalyst suffered exhaustive reduction at 300°C. This should not, however, lead to the conclusion that the activity of iron catalysts is essentially independent of their composition, but rather that highly active iron catalysts may be prepared in a number of different ways.

It will be seen from closer inspection of figures 8 to 11 that the character of the products formed during the different comparative experiments varied a good deal. Certain catalysts gave mainly solid paraffins; with others liquid hydrocarbons were the principal products. Moreover, the catalysts are distinguished by their tendency to promote either olefin formation or the formation of alcohols and esters. Whereas converters 1 and 6 gave products very similar to those obtained with cobalt catalysts, the catalysts in converters 2 and 5 gave large amounts of alcohols. Figure 8 shows the amounts and composition of the solid paraffins obtained per day in a single stage for a 10-cubic meter converter, figures 9 and 10 give the corresponding values for the Diesel oil and gasoline fractions, respectively.

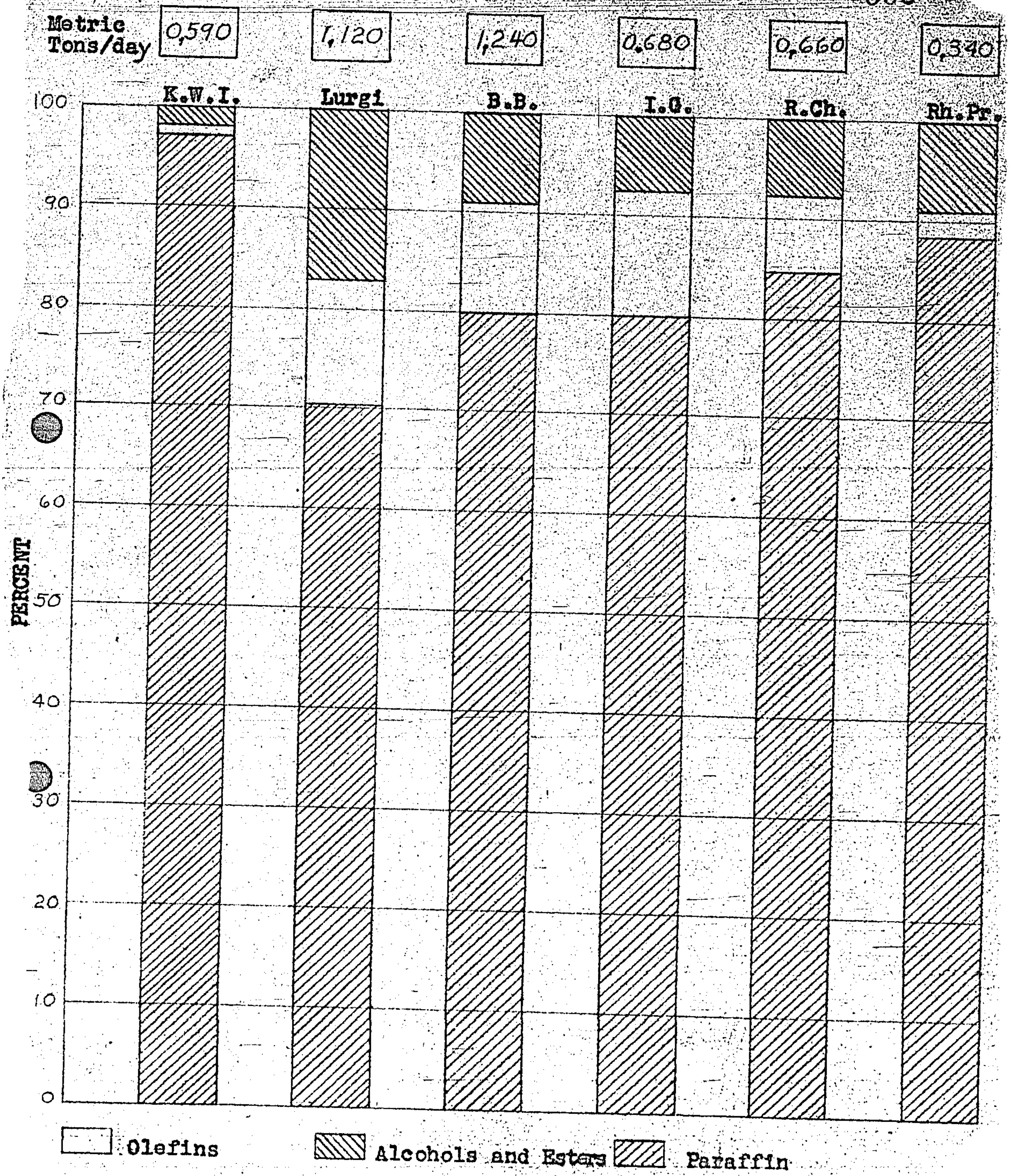


Figure 8: Paraffin production and composition in the Schwarzheide tests (single stage).

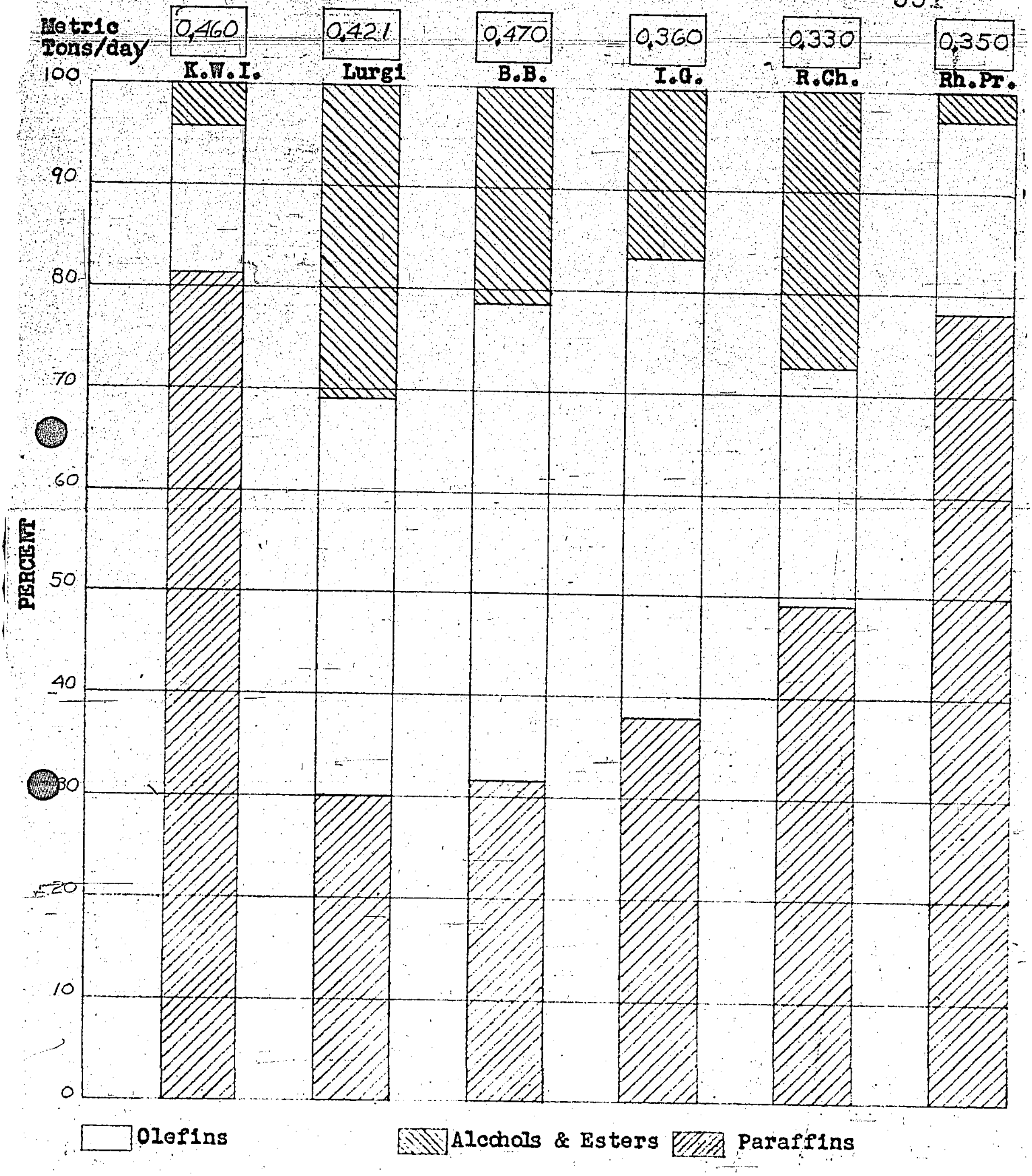


Figure 9: Diesel oil production and composition in the Schwarzheide tests (single stage).

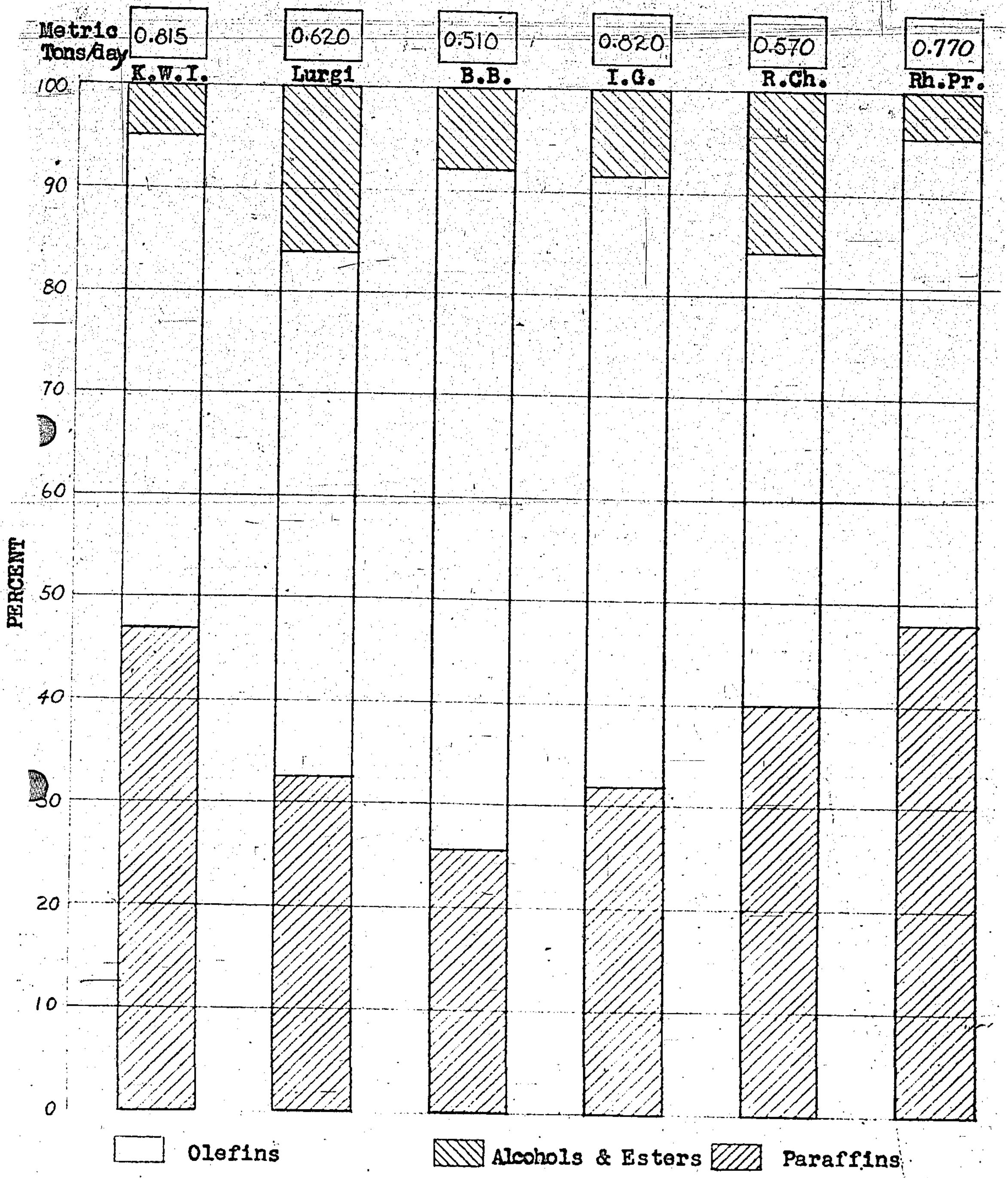


Figure 10:- Benzine production and composition in the Schwarzheide tests (single stage).

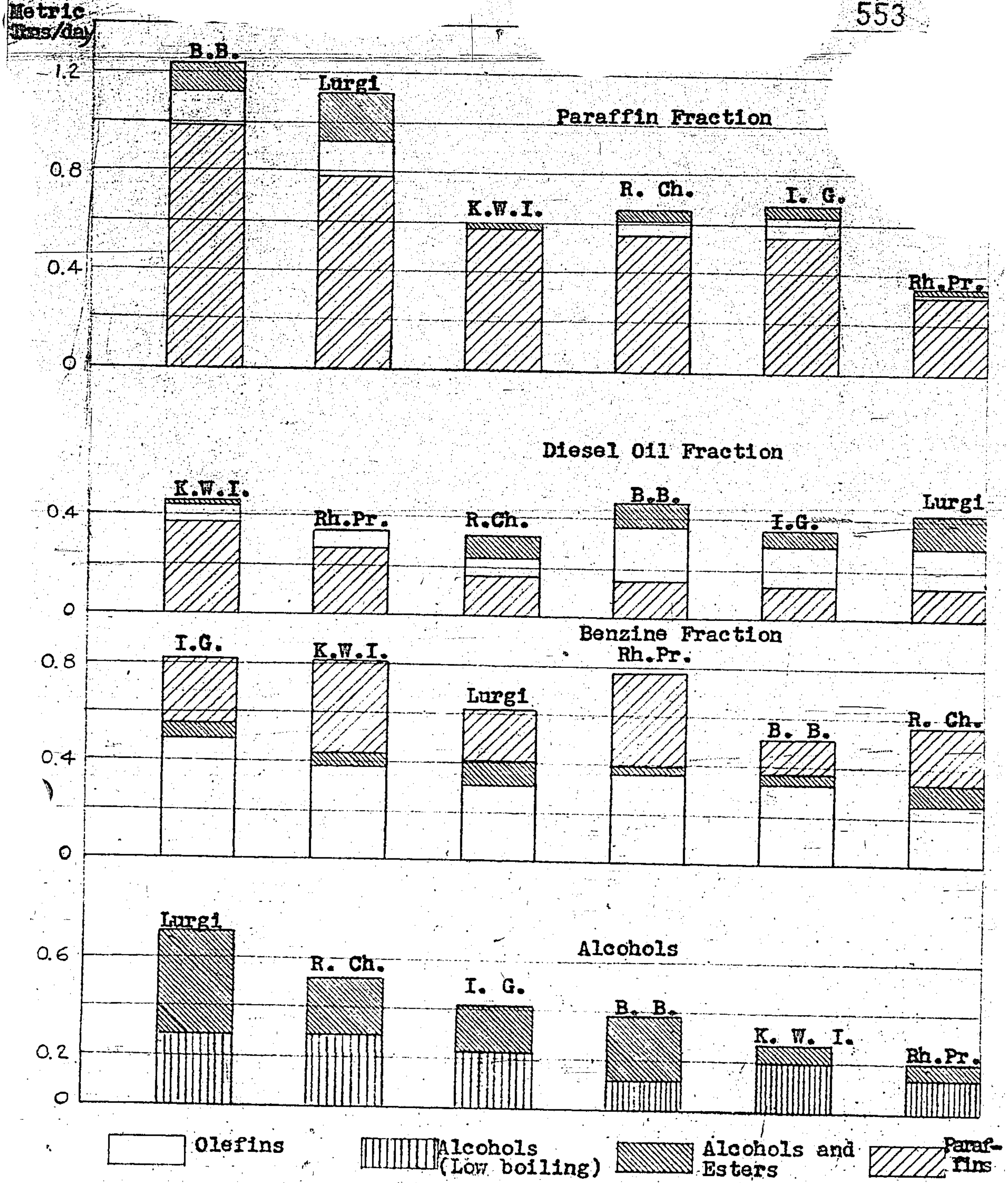


Figure 11: Comparative values of the Schwarzheide catalysts for the production of various materials (single stage).

An evaluation of the experimental results in terms of the products formed will be found in figure 11. For the paraffin fraction, the different experiments are listed in order of the formation of saturated paraffins (in tons per day). Since the products having the highest content of saturated hydrocarbons also give the highest cetene numbers, a similar system was used for the Diesel oil fraction. The gasolines were listed according to the amounts of olefins plus alcohols ~~formed. Finally, a comparison of the oxygenated compounds formed dur-~~ ing the different experiments was made. These compounds consist mainly of alcohols whose lower members are soluble in the water from the reaction and whose higher members are soluble in the hydrocarbons formed.

A study of branch chain formation (Dr. Koch, KWI) showed that 11 to 15 percent of the hydrogenation products of the C_6 fraction and 11 to 18 percent of those belonging to the C_7 fraction were branched-chain hydrocarbons. This study was carried out by means of a 1 meter "Spinning-Band" column (40 theoretical plates). The branched-chain hydrocarbons of the C_6 fraction consisted almost exclusively of 2- and 3- methylpentane and those of the C_7 fraction of 2- and 3-methylhexane.

Conclusions

The results of the comparative experiments at Schwarzheide show that it is possible to substitute an iron catalyst for a cobalt catalyst. The average capacity in tons per day was approximately the same as for cobalt catalysts. However, the ratio in which carbon monoxide and hydrogen react does not correspond to the carbon monoxide-hydrogen ratio of the water gas employed as synthesis gas. As a result, the yields obtained per normal cubic meter of synthesis gas, or of carbon monoxide-hydrogen mixture, for the single stage, were lower than is the case with cobalt catalysts, or than appears desirable for industrial economy. (See Table 16, 1-4.) Increased carbon monoxide conversion, either by treating the end gas from the six experiments in a second stage, or by reducing the rate of flow, would not give the desired results, since in most of the experiments carbon monoxide conversion is already extensive, and the large excess of hydrogen in the end gas cannot be eliminated in this way. Extrapolation of the yields for a 95 percent conversion of carbon monoxide leads to the values given in Table 16, 5. Only the Rh.Pr. catalyst, which gave the lowest conversion obtained at Schwarzheide (including oxygen compounds, excluding C_1 and C_2, see 3), and consequently the lowest yields, reached an extrapolated value of 150 grams per normal cubic meter ($CO + H_2$). However, in this particular experiment it is accompanied by a considerable drop in space-time yields. It was observed in special experiments at Schwarzheide that, for 90% carbon monoxide conversion (based on C_3 and more, including alcohols) these space-time yields amounted to 2.57 tons per day for converter 1, 2.77 tons per day for converter 2, 2.26 tons per day for converter 3, 2.41 tons per day for converter 4, 1.76 tons per day for converter 5, and 1.49 for converter 6. An extrapolation of this type, such as is found in a great variety of reports, is not permitted here owing to the fact that an increase in carbon monoxide conversion is accompanied by a change in the nature of the products. Had the object of the Schwarzheide experiments been to obtain maximum yields by a two-stage operation (without intermediate regeneration of synthesis gas from the gaseous products formed in the first stage), then the amount of carbon monoxide conversion in the first stage and (formation of gaseous compounds) would have been lower. In experiment 6, carbon monoxide conversion could not be increased above 62 percent due to the fact that the upper temperature limit was reached.

The gaseous hydrocarbons (C_1 + C_2) obtained by a single stage operation (Table 16) could be reacted with the carbon dioxide of the exit gas and the resulting CO - H_2 mixture passed over a water gas shift catalyst. Scrubbing out the carbon dioxide thus produced would result in a water gas with the same carbon monoxide-hydrogen ratio as used initially. A second stage of operation under conditions similar to those used in the single stage would give the total yields shown in the horizontal columns 6 to 8. Operation in two stages gives as much as 180 grams of hydrocarbons with 3 or more carbons per molecule including oxygenated compounds. If oxygenated compounds are not included, 160 grams of the same type of hydrocarbons are obtained.

An increase in yield for the two-stage operation could be brought about by adjusting the carbon monoxide-hydrogen ratio of the synthesis gas to the consumption. The use of a carbon monoxide-rich synthesis gas gives higher yields and promotes the formation of olefins, but it requires higher operating temperatures and increases the risk of carbon formation, particularly in the case of fixed catalyst beds. On the other hand, if the synthesis is conducted in a single stage with recycling (see recycle experiments) increased water formation would serve to shift the carbon monoxide-hydrogen ratio towards hydrogen, thus favoring the course of conversion.

It should be observed that a possible procedure for the synthesis would be to operate with an iron catalyst in a first stage and with a cobalt catalyst in a second stage. Starting with standard water gas, it is possible to operate in such a way in the first stage that in the second stage the synthesis gas has a composition optimum for use with a cobalt catalyst ($1CO + 2H_2$).

As will be seen from the composition of the products shown in the various figures, some of the results fall far short of the specified condition that the products formed be similar to those synthesized with cobalt catalysts, for example, paraffin and Diesel oil fractions consisting essentially of saturated normal paraffins and no appreciable amount of alcohol. On the other hand the variety of the compounds obtained does show that it is possible to control the composition of the products by selecting iron catalysts of suitable composition.

F. Synthesis with Highly Active Iron Catalysts at Medium and Normal Pressures

A constantly recurrent problem is that of the industrial use of iron catalysts for synthesis at normal pressure. In recent years, research work in this field seems to have made progess.

Table 16. – Schwarzheide Experiments. Yields (Grams per Normal Cubic Meter)

A. Single Stage Procedure	Based on	KWI	L	BB	IG	RCh	Rh.Pr.
1. Total yields (incl. C_1, C_2, and O)	Synthesis gas with 88% ($CO+H_2$)	125.1	124.4	108.3	117.1	103.1	104.0
2. Total yields (incl. C_1, C_2, and O)	($CO+H_2$)	142.2	141.4	123.1	133.1	117.2	118.0
3. Yields (incl. O, excl. C_1 and C_2)	($CO+H_2$)	116.8	125.7	112.6	110.8	101.2	98.0
4. Yields (excl. C_1, C_2 and O)	($CO+H_2$)	115.3	119.0	109.5	106.8	95.7	95.8
B. Extrapolation to 95% CO Conversion							
5. Yields (incl. O, excl. C_1 and C_2)	($CO+H_2$)	133	136	139	130	136	150
C. Two Stage Procedure, with Conversion of C_1 and C_2							
6. Yields (incl. O, excl. C_1 and C_2)	($CO+H_2$)	177	180	166	165	156	151
7. Yields (excl. C_1, C_2 and O)	($CO+H_2$)	171.5	170.4	161.1	158.9	147.5	147.6
8. Yields (excl. C_1, C_2, alcohols and esters)	($CO+H_2$)	160	135	142	140	119	136

At the Mülheim Institute for Coal Research, Pichler and Weinrotter developed a new series of iron catalysts in addition to those already mentioned. An iron catalyst considerably more active for both medium- and normal-pressure synthesis than the catalysts compared at Schwarzheide was prepared from a chloride solution by precipitation with sodium carbonate and pretreatment with synthesis gas at atmospheric pressure.

For example, let us consider preparation of a catalyst obtained from an iron solution containing ferrous and ferric iron in a ratio of 3 : 1, plus 20 percent of copper:

KWI, Catalyst N 75

$75\ Fe^{+2} - 25\ Fe^{+3} - 20\ Cu - 1\ K_2CO_3$

Solution 1, the following constituents dissolved in 2 liters H_2O

134 grams $FeCl_2 \cdot 4H_2O$	(37.5 grams Fe)
61 grams $FeCl_3 \cdot 6H_2O$	(12.5 grams Fe)
26 grams $CuCl_2 \cdot 2H_2O$	(9.2 grams Cu)

Solution 2,

200 grams Na_2CO_3, dissolved in 2 liters H_2O. Solution 1 is heated to 70°C. and solution 2 to boiling. Precipitation is effected by adding solution 2 to solution 1 as rapidly as possible until a slightly alkaline reaction persists. The precipitate is washed free of alkali on the suction filter (for instance, with 9 x 800 cubic centimeters of boiling water). The washed catalyst is mixed

to a paste with boiling water and is alkalized with 0.5 gram of K_2CO_3 dissolved in 100 cubic centimeters of water, added with stirring on the water bath. This mixture is evaporated on the water bath to a fairly thin paste and dried at 105°C. for about 20 hours. After drying, the catalyst is broken up and screened to collect granules 2 to 4 millimeters in size.

Eighty cubic centimeters of catalyst were pretreated in a water-cooled laboratory converter with 40 liters per hour of mixed gas ($CO:H_2$ = 1:2) at atmospheric pressure and 225°C., the reaction tube having an inside diameter of 10 millimeters. After 48 hours it was necessary to remove, by extraction with synthesis oil (Diesel oil boiling between 230 and 280°), the paraffin collected in the catalyst. Pretreatment was continued, under the same conditions, for another twenty-four hours. After a second extraction, the catalyst was ready for use in synthesis.

For synthesis at atmospheric pressure, a space velocity of synthesis gas (water gas) of 100 at 220°C., or 50 at 210 to 212°C., may be used. A catalyst with the alkali content of the example described above must be freed of paraffin by extraction every 2 or 3 days (under certain circumstances, extraction could be continuous).

Over a long period of operation, the tendency of the catalyst to form solid paraffins gradually decreases and the intervals between extractions can be lengthened progressively. In each case, a drop in the contraction values indicates that an extraction has become necessary. Catalysts with a lower alkali content produce less paraffin and do not require such frequent extractions.

With a space velocity water gas of 50 at 211°C. and atmospheric pressure, 135 grams of products per normal cubic meter of ($CO + H_2$) was obtained for a single stage. The products were distributed as follows (catalyst with 1% K_2CO_3):

Fraction	Weight Percent
CH_4	2.4
$C_2 - C_4$	10.1
Liquid hydrocarbons boiling below 180°C.	13.5
Liquid hydrocarbons boiling above 180°C.	74.0
	100.0

For synthesis at 10 atmospheres with a space velocity of 100 at 200°, the same catalyst gave 137 grams of products per normal cubic meter of ($CO+H_2$). Extraction is not necessary at this pressure. The life of the catalyst is very long. During the first month of operation, the products had the following composition:

Constituent	Weight Percent
CH_4	3.2
$C_2 - C_4$	9.0
Liquid hydrocarbons boiling below 180°C.	10.0
Liquid hydrocarbons boiling above 180°C.	77.8
	100.0

In order to obtain a high degree of activity in medium-pressure synthesis, the catalyst had to be pretreated with synthesis gas at atmospheric pressure.

This experiment was carried out at the Mülheim Institute for Coal Research in a pilot plant synthesis apparatus of the type used in the Schwarzheide experiments (10 atmospheres, 201°C., 88% CO conversion, 135 grams of C_3+ hydrocarbons per normal cubic centimeter in a single stage with no recycle). It was possible to operate in such a way that 37 percent of the yield was hard paraffins boiling above 450°, with no intermediate extraction necessary.

Catalyst N50

$$50\ Fe^{+2} - 50\ Fe^{+3};\ 1\%\ Cu,\ 1/4\%\ K_2CO_3$$

An iron catalyst of the above composition prepared under the conditions described on page 76 produced a lower paraffin yield for the same degree of conversion and the same total yield. At atmospheric pressure this catalyst was extracted once a week. As with N 75, no extraction was necessary at medium pressures.

Over the range studied with the highly active KWI catalysts, N 50 and N 75, the rate of the reaction in volumes of gas per hour, doubled for a rise in temperature of 10°. In contrast to the cobalt synthesis, for the region between normal and medium pressure synthesis, the percentage of gas conversion increased with the increasing pressure, so that from atmospheric pressure to 10 atmospheres the conversion increased 4 to 5-fold. The upper pressure limit would correspond to the beginning of carbonyl formation at 20 to 30 atmospheres (see figure 12). At atmospheric pressure and 220°C., the highly active catalysts described above gave approximately the same gas conversion and yields as at 10

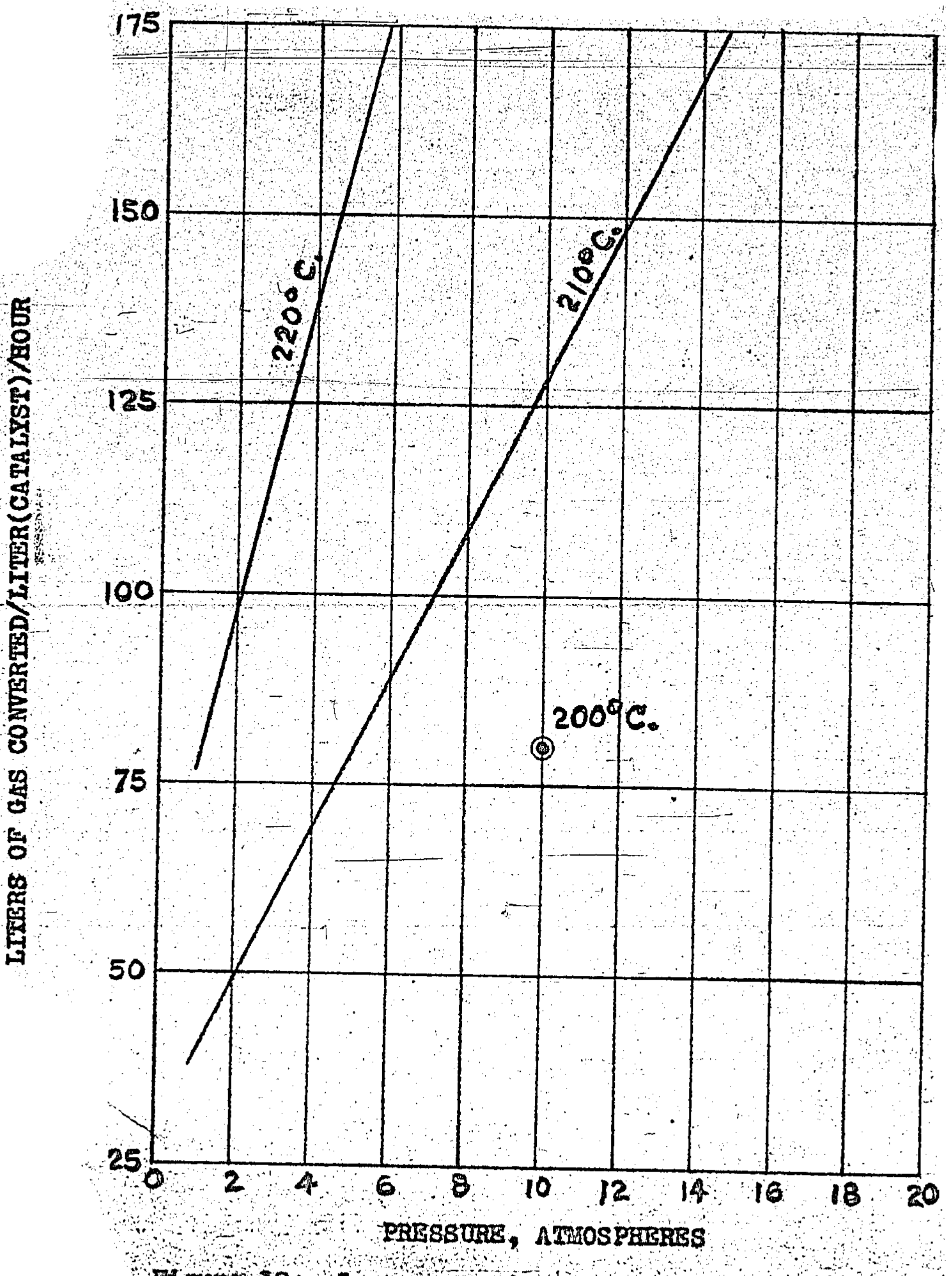


Figure 12: Gas conversion on an active iron catalyst at various pressures.

atmospheres and 200°C. Although the solid paraffin fraction was smaller at atmospheric pressure, frequent extraction was nevertheless necessary; this was not the case at medium pressure.

In recent years, normal-pressure experiments with iron catalysts have also been conducted in the laboratories of the commercial plants, for instance at Rheinpreussen. According to H. Koelbel 2-stage operation with a synthesis gas containing 1CO + 1.7 to 2.2 H_2, at a temperature of 215 to 225°, gave yields of 120 to 125 grams of C_5+ (150 grams of C_2+). Under these conditions, which included a 1:3 gas recycle in the first stage, oxygen from the carbon monoxide is said to give mainly water. However, it is necessary to recycle large volumes of gas at atmospheric pressure which reduces the economic value of this procedure. The average throughput for a 10-cubic converter, is calculated to be 700 cubic meters per hour (space velocity 70).

The experimental results given in the present section show that the development of iron catalysts has by no means reached the final stage and that the problem of operation at normal pressure should not be overlooked.

G. Recycle Experiments

In discussing cobalt synthesis at medium pressure, two points were emphasized in connection with recycling: (1) the gas recycled over the catalyst has a high carbon monoxide:hydrogen ratio; (2) the synthesis operates smoothly with a high throughput of synthesis gas diluted by a large amount of inert components. In the cobalt catalyst synthesis, the first point was a controlling factor for the formation of products with a high olefin content. The iron catalyst synthesis differs from synthesis with cobalt catalysts in that a larger amount of oxygen from carbon monoxide appears as carbon dioxide and alcohols. In the recycle process the shortened contact time on the catalyst of the products that condense at room temperature results in a change in the consumption ratio of carbon monoxide and hydrogen. Owing to the increased rate of gas flow, the water which forms the primary byproduct in the synthesis does not have time to undergo the water gas shift reaction with carbon monoxide, as is the case at the usual gas velocity. In the Schwarzheide experiments (single pass) with the exception of experiment 6, a CO - H_2 consumption in the ratio of 1 : 0.7-0.8 was obtained. For a recycle ratio of 1 part of fresh gas to 2.5 parts of recycle gas, a synthesis gas containing 1 part of carbon monoxide to 1.2 - 1.3 parts of hydrogen can easily give a CO - H_2 consumption ratio of 1 : 1.1 - 1.2. In this way, with a 1 : 2.5 recycle, a CO - H_2 consumption corresponding to the composition of water gas may be obtained. However, if extensive consumption of the carbon monoxide-hydrogen mixture is required, the recycle stage should as a rule be followed by a second, single-pass, stage in which the gas consumption that is normal for a single stage is obtained.

Two recycle experiments in the medium pressure synthesis with iron catalysts (Lurgi) are described below (figure 13). The first experiment was carried out at 230°C., the second at 275°C. Corresponding to the difference in the temperatures, iron catalysts that differed in activity were used (see chapter on "Reaction Conditions and the Catalyst", p. 55). At 230°, the non-aqueous products comprised 60 percent of paraffin and 20 percent of gasoline; at 275°, 8 percent of paraffin and 71 percent of gasoline. Diesel oil was present to the extent of 20 to 21

Table 17.--230° C.

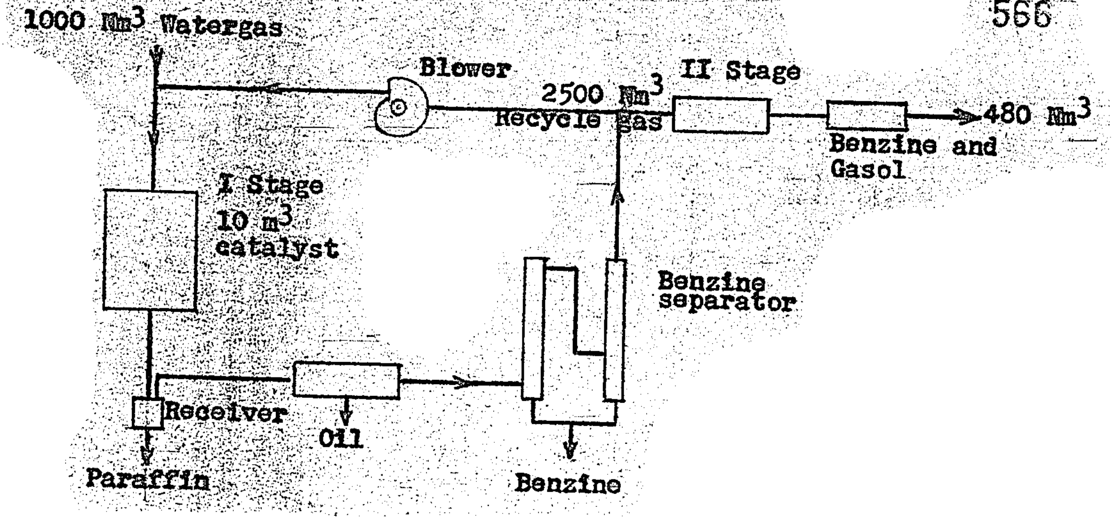


Table 18.--275° C.

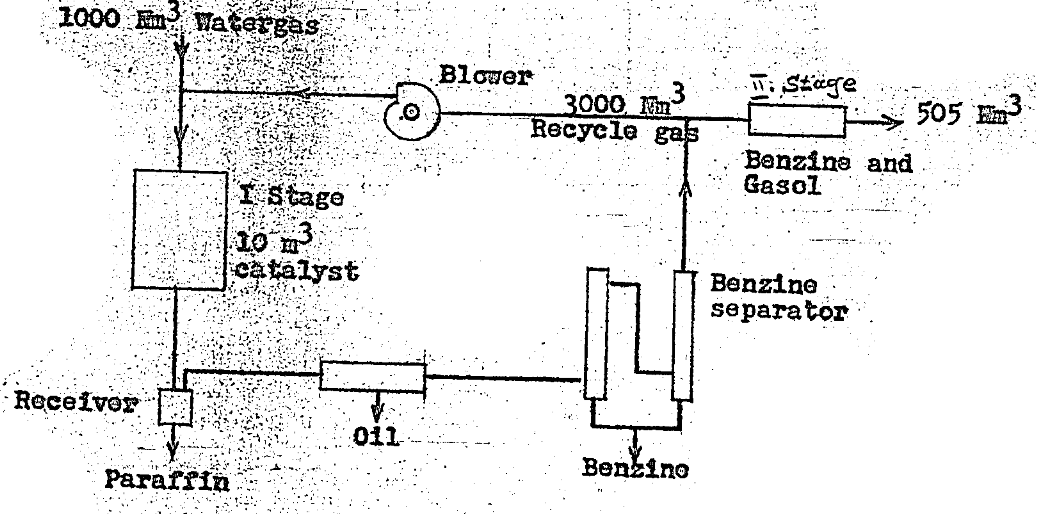


Figure 13: Schemes for recycle experiments of Tables 17, 18.

percent. The gasoline from the 230° experiment (Table 17) contained 60 percent of olefins, as against 75 percent in the 275°-experiment (Table 18). The corresponding olefin content of the Diesel oil fractions amounted to 45 and 60 percent, respectively. The gaseous hydrocarbon (C_1 to C_4) fraction was 18 percent 230° and 40 percent at 275°.

Table 17. - Recycle Experiment at 230°

Operating conditions: pressure, 20 atmospheres; temperature, 230°C.

Catalyst: 100 Fe - 25 Cu - 9 Al_2O_3 - 2 K_2O - 30 SiO_2

Yield:

First stage: 136 Kg/1000 Nm^3 ideal gas
(Second stage hypothetical): total yield 170 Kg/1000 Nm^3

Product distribution, Kg:

Hard paraffin	66
Paraffin	22
Oil	29
Gasoline	29
Additional alcohols	9
Gasol	15
Total	170 Kg. (excluding CH_4)

Gas analyses data, percent:

	Fresh Gas	Converter In-Gas	End Gas
CO_2	5.8	22.9	28.2
CO	37.6	26.9	22.6
H_2	48.1	31.8	27.0
CH_4	0.1	2.0	2.7
C_nH_m	--	1.4	1.9
N_2	8.4	15.0	17.6

Table 18. - Recycle Experiment at 275°C.

Reaction conditions: pressure, 20 atmospheres; temperature 275°C.

Catalyst: Lautamasse (iron hydroxide residue from aluminum extraction) impregnated with 3% Cu.

Composition of Lautamasse: 50% Fe_2O_3, 11-12% Al_2O_3, 3-4% Na_2O, 7-8% TiO_2, 4-5% SiO_2, 8-9% CaO, 1-2% MgO, 0.1-0.2% MnO, 0.8-1.0% SO_2, 0.3-0.8% P_2O_5.

Yield (135 Kg/1000 Nm^3 ideal gas):

Paraffin	8
Oil	20
Gasoline	70
Additional alcohols	5
Gasol	32
Total	135 Kg. (excluding CH_4)

Gas Analyses Data, Percent:

	Fresh Gas	Converter In-Gas	End Gas
CO_2	2.8	31.6	48.0
CO	53.2	29.8	16.7
H_2	35.6	19.8	11.3
CH_4	0.1	3.5	5.3
C_nH_m	-	1.3	2.2
N_2	8.3	14.0	16.5

A recycle experiment at medium pressure with an iron catalyst also served as the basis for the so-called "Arezzo" project at the Ruhrchemie. An extruded iron Ruhrchemie catalyst was operated over a period of 4 months, at 20 atmospheres and 250 to 257°C., with a 1 : 2.5 ratio of fresh to recycle gas. Table 19 shows the composition of the synthesis gas (water gas) and that of the tail gas from the first stage (53.2 percent contraction). It also shows the gas composition at the end of a hypothetical second stage (total contraction 68.5%).

Table 19. - Gas Analyses for the Arezzo Project

	CO_2	CO	H_2 (Percent)	CH_4	N_2
Water gas	4.5	39.0	50.0	3.5	3.0
End gas, first stage	23.8	25.0	32.0	12.8	6.4
End gas, second stage	41.0	12.4	15.9	21.2	9.5

The ratio of hydrogen to carbon monoxide in the fresh gas was 1.28 : 1. Since the consumption ratio was adjusted to the hydrogen-carbon monoxide ratio in the synthesis gas, extensive reaction of carbon monoxide and hydrogen is to be expected, without gas adjustment between the stages. It is desirable to scrub out carbon dioxide between the stages for better operation of the synthesis, but this is a matter of economy. The yield of hydrocarbons containing three or more carbons per molecule amounted to 116.5 grams per normal cubic meter of (CO_2+ H_2) for the first stage. Based on 90 percent conversion of carbon monoxide conversion (two stages) a yield of 148.5 grams per normal cubic meter was assumed. The amount of gasol produced during the first 20 days of this experiment increased from 9 to 20 percent by weight, that of gasoline from 33 to 40 percent, that of oil (200 to 320°) from 15 to 16 percent, whereas the quantity of paraffin dropped from 43 to 32 percent. The fraction of gasoline boiling below 200° contained 66 percent by volume of olefins; oil boiling from 200 to 320°, 52 percent.

H. Occurrence of Oxygenated Compounds, Particularly Alcohols, During Synthesis; OXO and the Synol Syntheses

Early in this manuscript, mention was made of the discovery by Franz Fischer and Hans Tropsch, in 1922 and 1923, of the synthesis of synthol, a mixture of widely oxygenated organic compounds, obtained from water gas in the presence of alkalized iron catalysts at high pressures and temperatures of about 400°C.

The fact that small amounts of oxygenated organic compounds form in conjunction with hydrocarbons in the Fischer-Tropsch synthesis at normal pressure, has been known since the earliest days of the process.

35/ Fischer, F., and Tropsch, H., Brennstoff Chem., vol. 7, 299, 1926.
36/ Fischer, F., and Tropsch, H., Brennstoff Chem., vol. 9, 21, 1928.
37/ Fischer, F., and Koch, H., Brennstoff Chem., vol. 13, 429, 1932.
38/ Koch, H., Pichler, H., and Kolbel, H., Brennstoff Chem., vol. 16, 382, 1935.

In normal pressure synthesis with cobalt catalysts, oxygenated organic compounds represent only a very small quantity of byproduct. Nevertheless, the fact that such oxygenated compounds are produced suggested to various investigators that oxygenated compounds are intermediate in the hydrocarbon synthesis.

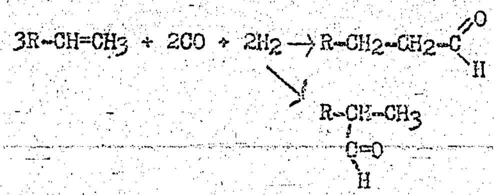
39/ Elvins and Nash, Fuel Sci., vol. 5, 263, 1926.
40/ Elvins and Nash, Nature, vol. 118, 154, 1926.
41/ Smith, Hawk, and Golden, Jour. Am. Chem. Soc., vol. 52, 3221, 1930.

As long as the production of motor fuels constituted the sole purpose of the synthesis, Franz Fischer and his collaborators strove to keep at a minimum the formation of oxygenated compounds. Under normal conditions, the water resulting from synthesis over a cobalt catalyst contained 0.35 percent of fatty acids (mainly acetic acid); fatty acids in the C_5 to C_{10} range were present to the extent of 0.06 percent in the liquid hydrocarbons. The aqueous fractions from cobalt medium-pressure synthesis contained about 1 percent of oxygenated organic compounds, chiefly alcohols. Some of these were recovered in the German synthesis plants in recent years by suitable fractionation.

The situation changed in Germany when, in addition to the production of fuel, the synthesis of fatty acids and alcohols, detergents, plasticizers, and of fats became important. The oxidation of synthetic paraffins boiling between 320° and 450°C. (at atmospheric pressure) was undertaken. Paraffins obtained in the medium-pressure synthesis (C_{20} to C_{40}) appeared particularly suitable for this purpose. According to Imhausen, (Witten/Ruhr) these molecules are split in half during oxidation, resulting in the production of the desired C_{10} to C_{22} fatty acids. The careful cracking of higher-melting paraffins results in paraffins suitable for oxidation. Production of soap, detergents, and synthetic "butter", from synthetic paraffins was carried out on an industrial scale by the "Märkische Seifenindustrie" at Witten/Ruhr. The fraction boiling in the range from 280° to 320°C. was sent to the I.G. Farbenindustrie A.G., where it was sulfochlorinated to produce detergents.

In 1938, a process was developed at the Ruhrchemie A.G. in which aldehydes were produced by addition of carbon monoxide and hydrogen to olefins at relatively low temperatures (50° to 200°C.) and high pressures. (See also Smith, Hawk, and Golden, Jour. Am. Chem. Soc., vol. 52, 3221, 1930, according to whom synthesis gases containing ethylene produce oxygenated products at ordinary pressure.)

The reaction proceeds according to the following general equation:



$$3R-CH=CH_3 + 2CO + 2H_2 \rightarrow R-CH_2-CH_2-C\genfrac{}{}{0pt}{}{/\!\!/ O}{\diagdown H}$$

$$\searrow \begin{array}{l} R-CH-CH_3 \\ \quad\; | \\ \quad C=O \\ \quad\; \diagdown H \end{array}$$

Cobalt is the catalyst which is used (essentially cobalt carbonyl). Nickel is not suitable. The aldehydes may be reduced directly to alcohols, or oxidized to fatty acids.

Reppe (I.G.) has also developed a process by which addition of carbon monoxide and water to olefins results in the direct formation of fatty acids.

Pichler and Büffleb[42] obtained high yields of formic acid by reaction of carbon monoxide and water in the presence of strong acids. The addition of carbon monoxide to methanol and higher alcohols results in the formation of acetic acid and the corresponding higher acids. A series of patents, particularly those of the Dupont Company, relates

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[42] Pichler, H., and Buffleb, Brennstoff Chem., vol. 23, 73, 1942.

to processes of this type. Experiments in this field were also conducted at the Mülheim Institute. Theoretically it should be possible to obtain a fatty acid with any given number of carbon atoms from carbon monoxide, water, and hydrogen by alternate addition of carbon monoxide and reduction of the acid formed to the corresponding alcohol. In practice, however, the side reactions make such a procedure impractical.

The olefins necessary for the new process, known as OXO synthesis, may be obtained in the medium-pressure synthesis with iron catalysts or by recycling with carbon monoxide-rich synthesis gas in medium-pressure synthesis with cobalt catalysts. Starting from carbon monoxide and hydrogen and a suitable fraction of the olefins, it is possible to obtain any desired aldehydes, alcohols, and fatty acids.

As the hydrocarbon synthesis at medium pressure in the presence of iron catalysts results in the formation of considerable amounts of alcohols as primary synthesis products, the question was again raised of a direct synthesis of alcohols from carbon monoxide and hydrogen. In the Schwarzheide experiments with iron catalysts at medium pressure, discussed in detail earlier in this report, between 10 and 30 percent of the liquid and solid products were comprised of alcohols and esters (principally alcohols) notwithstanding the stipulation that the products formed be as similar as possible to those obtained with cobalt catalysts at medium pressure (where only small amounts of oxygenated organic compounds are produced). In medium-pressure synthesis with iron catalysts, the formation of as much as 30 percent of alcohols was unavoidable at 10 atmospheres and 220°C.

Operating at 10 atmospheres and 205°C. with a precipitated catalyst of composition 100 Fe - 5 Cu - 10 CaO - 5 Kg, alkalized with 3 percent of potassium hydroxide, and reduced by hydrogen (325°, 24 hours, 85 percent reduction), Roelen (Ruhrchemie) obtained liquid products containing as much as 52 percent of alcohol.

At this low reaction temperature, the catalyst had only a short life, but the KWI catalysts, N 50 and N 75, prepared under the same conditions, were operated for a long time at 200° and 10 atmospheres.

It was known that an increase in the synthesis pressure resulted in increased production of oxygenated reaction products.

Over a period of years, particularly after the work of Franz Fischer and his collaborators had led to industrial-scale operation, the synthesis of hydrocarbons from carbon monoxide and hydrogen was the subject of various research projects in different laboratories of the I.G. Farbenindustrie. It was found that after careful reduction, fused catalysts of the synthetic ammonia type can be used in the medium-pressure synthesis. The Ruhrchemie and the I.G. collaborated on the OXO synthesis, particularly with respect to further use of the OXO products. However, at the I.G. Farbenindustrie, the numerous variations in the use of iron catalysts suggested a possible process for the direct synthesis of alcohols, which would be shorter than the procedure involving intermediate olefins and the OXO synthesis.

The fact that the alcohol content of the liquid products from the medium-pressure iron synthesis is higher at low temperatures than at higher temperatures served as the starting point for a process to which the I.G. gave the name of Synol synthesis. The differences in the synthesis products is immediately apparent by comparison with the experiments carried out by Breywisch (Table 20). The first of these experiments was conducted with a precipitated catalyst (18.4% SiO_2, 35.3% Fe_2O_3, 0.8% Al_2O_3, 9.4% MgO, 2.8% K_2O, 6.4% CuO, and 4.7% NO_3). The second experiment was carried out with a standard fused catalyst, properly reduced. In both cases a relatively low yield of 63 grams per cubic meter was obtained at 220 to 222° in experiment 1, and at 191 to 199° in experiment 2. These are normal operating temperatures for synthesis at medium pressure with iron catalysts.

Examination of the fractions of product shows that the alcohol content is greater in experiment 2 than in experiment 1, especially for the higher boiling fractions. The reaction has been represented by the general equation

$$25\ CO + 23\ H_2 \rightarrow CH_3(CH_2)_3\ OH + C_8H_{16} + 11\ CO_2 + 5\ H_2O.$$

As already shown in the discussion of the iron medium pressure synthesis, shortening the contact time of the gas in the converter, for instance, by recycling, increases the amount of water formed at the expense of the secondary byproduct carbon dioxide. In the same way, prolonged contact with the catalyst converts alcohols into hydrocarbons. For this reason, it is advisable to avoid excessively thick catalyst layers and to operate in several stages (3-4) with removal of the major part of the reaction products after each stage. Operation at low temperatures is facilitated by keeping the partial pressure of inert components as low as possible (removal of carbon dioxide). As already indicated, high pressure is desirable up to the pressure (25 atmospheres) at which carbonyl formation begins.

Table 20. - Formation of Alcohols in Iron Medium Pressure Synthesis

Experiment	1		2	
Reduction conditions	24 hours, 230°C.		2-1/2 days, 500°C.	
Space velocity of H_2 synthesis	1000		3000	
Synthesis Gas-throughput	350		350	
Conversion, $m^3 CO+H_2/m^3$ catalyst/hr.	150		150	
Yield, g/m^3	65		65	
Synthesis temperature °C.				
After 10 days	220		191	
After 20 days	222		192	
After 30 days	222		193	
Distribution of products, percent	10th-13th day	13th-30th day	7th-17th day	20th-30th
Gasol	16.9	12.3	13.1	15.3
<200°	34.4	43.9	50.0	43.6
200 - 230°	4.6	3.5	2.2	3.8
230 - 350°	18.4	12.3	16.5	11.4
350 - 400°	3.8	6.1	4.3	8.1
>400°	21.9	21.9	13.9	17.8
Alcohol content of the fractions				
<200°	29.4	26.4	29.5	34.6
- 230°	26.0	16.6	34.5	35.7
- 350°	36.4	26.9	53.5	59.8
- 400°	37.5	21.7	37.5	56.5
>400°				
Olefin content of the fractions				
<200°	13.2	40.2	45.0	42.0
- 230°	37.2	48.8	35.0	34.3
- 350°	19.5	40.2	27.9	24.8
- 400°	18.2	31.4	24.4	28.1
>400°				

In order to operate at low temperatures, pretreatment of the catalyst is necessary, as for example, by the I.G. Farbenindustrie method of reducing the catalyst at 400 to 500°C. with a high space velocity (1000) of hydrogen. Since low synthesis temperatures are necessary for the production of high alcohol yields, precipitated catalysts are in principle most suitable owing to their large surface area. However, the I.G. recommends one of its own fused catalysts for this purpose.

In conclusion, the following conditions may be listed as promoting alcohol formation in medium pressure synthesis with iron catalysts:

1. Low synthesis temperatures.
2. High pressures.
3. Low inert gas and carbon dioxide content.
4. Synthesis gas with a high hydrogen content.
5. Short contact time of the gas over the catalyst.
6. Operation in several stages, preferably with recycling of gas and minimum conversion in each stage. (Carbon dioxide removal between stages).
7. It is reported that the potassium content of the catalyst should be 0.1 to 0.7 percent; using such a catalyst, an optimum alcohol content of 50 to 60 percent of the product may be obtained.

The I.G. had made plans for the construction of a larger plant (originally 10,000 tons per annum), whose main purpose was the production of alcohols as a source of detergents. However, it was found that the alcohols obtained by direct synthesis, in contrast to those obtained by OXO synthesis, were chiefly straight chain compounds; consequently the

OXO products were superior to the synol products as raw materials for detergents. As a result it was decided to operate the projected synol plant at somewhat higher temperatures, thus producing principally hydrocarbons for use as fuels. The synthesis converters were to correspond essentially to those of the Fischer Works.

The study of the constitution of alcohols formed by direct synthesis and by the OXO reaction was undertaken by Asinger and Berg, Leuna: The results obtained were summarized as follows:

1. Even when primary olefins (with double bond on end carbon) are used, the OXO reaction leads to the formation of mixtures of isomeric aldehydes, alcohols, or acids.
2. In general, the products formed are α- alkyl branched compounds, rather than α- methyl branched compounds. This has the effect of lowering the melting point of the OXO-fatty acid considerably and determines the hygroscopic capacity of the OXO-soap.
3. When primary olefins are used, the average amount of branched chain formation is about 50 percent.
4. The formation of branched chain compounds depends on double bond isomerization during the OXO reaction.
5. Double bond isomerization is initiated by cobalt carbonyl.
6. Isomerization and the OXO reaction proceed simultaneously, the latter probably being faster, so that formation of branched-chain products is not as extensive as would be

expected from the isomerization of olefins in the absence of hydrogen.

7. Iron carbonyl also promotes isomerization to some extent, but nickel carbonyl does not. The former observation is important in considering the composition of synol products.

8. In contrast to OXO alcohols, synol alcohols show virtually no branched chain formation.

9. It is extremely probable that the synol olefins form by dehydration of synol alcohols, and that their isomerization determined by the location of the double bond is caused by iron carbonyl. (TOM Reel 134, Section VII, Item 6, "Constitution of OXO and Synol Alcohols, August 21, 1942".)

Experiments, involving the dehydration of alcohols by stearic acid ester (without shifting of the double bond), splitting of the olefins by ozonization, and identification of the fatty acids by fractional distillation, provide a valuable clue to the relationship between synthesis at medium pressure and OXO synthesis. They show that the OXO reaction cannot be decisive in forming hydrocarbons from alcohols. This is also apparent from the fact that nickel, which is not suited as a catalyst for OXO synthesis, is an excellent catalyst for the synthesis of hydrocarbons. On the other hand, alcohols can be converted to hydrocarbons under the conditions prevailing in medium pressure synthesis, as is demonstrated by the fact that prolonging the contact time of the gas over the catalyst increases the hydrocarbon yield and decreases the alcohol yield. However, it cannot be concluded from such considerations that alcohols act as intermediates in the production of all hydrocarbons. There is no experimental evidence of an essential difference between the course of the reaction in medium pressure synthesis with iron catalysts and in the Synol synthesis.

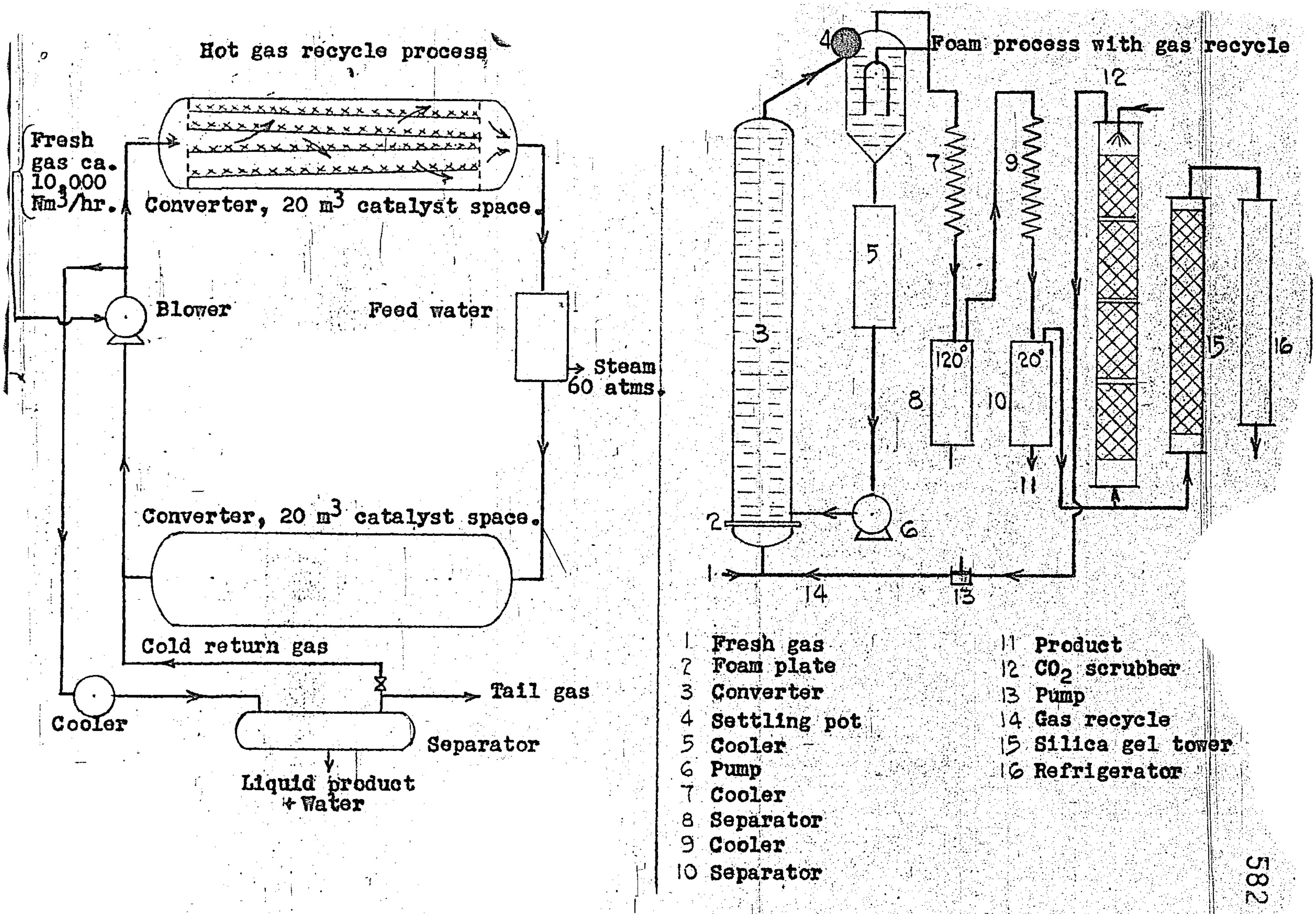
I. Modifications

a. Hot Gas Recycle

In contrast to the recycle process in which the ratio of fresh to recycle gas is generally between 1 : 2 and 1 : 3, and the condensable portion of the products is removed on leaving the converter (cold gas recycle), in the hot gas recycle process the ratio of fresh gas to recycled gas is about 1 : 100, and there is no separation of products (hot gas recycle). Whereas the former process is used to direct the course of the reaction in a certain manner and to permit higher gas throughput over the catalyst, the latter process is designed to remove exothermic heat of reaction from the fixed catalyst bed by external heat exchangers, with a large permissible temperature differential. The great quantity of heat liberated (700 calories per normal cubic meter of carbon monoxide-hydrogen mixture converted), and the low heat capacity of the gas, necessitate a high rate of gas circulation in this process. The problem of gas recycle was studied at the I.G. Farbenindustrie by Michael. He reports that when a temperature rise of 10° is allowed in the catalyst apparatus, the gas must be recirculated on an average of 100 times. One percent of fresh gas is added continuously to the recycle gas and the same amount was bled for removal of products and for eventual use in a second stage.

In general, sintered iron catalysts are used. The mechanical strength of precipitated catalysts is said to be insufficient to withstand the gas velocity required by the process. Also, at the high temperatures of operation, the high activity of precipitated catalysts leads to a considerable increase in the amounts of carbon and methane formed. According to Michael, fused catalysts cause resin formation.

At an operating pressure of 20 atmospheres, temperatures ranged between 300 and 325°. These relatively high temperatures, together with the high temperature differential in the fixed catalyst bed, necessary for economic reasons, increased the risk of localized carbon formation. Figure 14a shows a flow diagram of the hot gas recycle process; table 21 shows an analysis for a two-stage operation. In table 22, the second vertical column summarizes a hot gas recycle hydrocarbon synthesis experiment, whereas the third column shows a Synol synthesis experiment at a lower temperature. Because the hot gas recycle process has a tendency to form considerable quantities of gaseous hydrocarbons, the yields of liquid products reported by Michael are relatively high. It is true that the data given for the yields show rather wide variations. These yields were obtained in two to four stages, with removal of carbon dioxide between stages. It would appear that, as a rule, only the yields for the first stage were actually obtained, the results for the other stages being calculated or estimated. In pilot plant operations, it was found that the catalyst always had to be removed after a few weeks because of carbon deposition. Michael abandoned the hot gas recycle



Hot gas recycle process

Foam process with gas recycle

Figure 14: Schemes for the hot gas recycle and foam processes (Michael).

Table 21. - Hot Gas Recycle Process - Hydrocarbon Synthesis (1940)

	First stage	Second stage	Total
Space-time yield,			
Kg/liter catalyst/day	0.8	0.6	-
Conversion, percent	78	62	-
C_1+C_2 (saturated), percent	18	18	-
Yield, g/Nm^3(CO+H$_2$), primary products			
Ethylene	10.9	1.9	12.8
Propylene	13.0	2.2	15.2
Butylene	12.3	2.1	14.4
Crude gasoline	65.5	11.3	76.8
Middle oil	17.8	3.0	20.8
Alcohol	9.6	1.6	11.2
Paraffin	2.7	0.5	3.2
Total	131.8	22.6	154.4
Propane (C_3H_8)	3.4	0.6	4.0
Butane (C_4H_{10})	1.4	0.2	1.6
Complete total	136.6	23.4	160.0
Yield, g/Nm^3(CO+H$_2$) liquid products available (from polymerization at a rate of 97%) of			
Ethylene, C_2	10.0	1.7	11.9
Propylene, C_3 Butylene, C_4	24.2	3.9	28.1
Gasoline	65.5	11.3	76.8
Other products	30.1	5.1	35.2
Total	129.8	22.0	152.0

Gas Analysis Data

Constituent	Volume in-gas, liters	Volume exit gas, liters		
		First stage	Second stage	Final tail gas
CO+H$_2$	1000	220	66	66
N_2	30	30	30	30
CO_2	20	20	10	10
CO_2 produced	-	153	30	-
$CH_4+C_2H_6$	10	10	40	(40+6) -
CH_4 produced	-	30	6	-
C_2,C_3,C_4	-	25	(25+4) 29	-
Total	1060	488	211	152
Heating value, kilocalories	-	-	-	675

Table 22. - I. G. Experiments, Peters Report 1943

	High-Pressure Laboratory-Ludwigshafen Michael					Oppau Duftschmitt	
	2	3	4	5	6	7	8
	Gas Recycle						
Process	Hot Gas Recycle		Liquid-Phase Catalyst Suspension			Oil Recycle	
Type of Synthesis	Gasoline	Synol	Diesel Oil	Gasoline	Synol	Hydrocarbon Synthesis	Alcohols
Pressure, atmospheres	20	20	20	20	20	25	180
CO:H2 ratio	1:1.2	1:0.7	1:0.8	1:0.8	1:0.7	1:0.82	1:0.82
Temperature, °C.	325	195	240-250	300-310	210	240-290	235-280
Catalyst	Sintered iron	Synol catalyst	Iron-oxide powdered and reduced		Synol catalyst, fine	Fused iron catalyst	
Number of stages	2	4	3	3	4	2	3-4
Number of times CO_2 removed	1	3	2	2	3	0	2-3
Conversion, percent	91-92	90	ca. 90	ca. 90	90	87	ca. 90
Yield, g/Nm^3 $(CO+H_2)$, Primary products							
Oil	112	160	170	170	165	128	ca. 140
C_3+C_4(% olefins)	35(80)	15	5	5	12	22	ca. 50(65)
C_2(% olefins)	13	-	-	-	-	-	ca. 4(100)
C_1	35	10	6	10	6	20-30	-
Distribution of oil, percent							
to 200°C. (% alcohol)	78(30)	-	34	63	52	59(8)	?(ca. 45)
200-300°	-	-	-	-	17	12(2-3)	?(ca. 45)
300-350°	20	-	28	28	19	-	-
350-400°	-	-	-	-	-	29	?
over 400°	-	-	38	9	12	-	-
Space-time yield, Kg/l, catalyst/day	0.8	0.5	0.2	0.4	0.15	0.72	ca. 0.8
Gas space velocity m^3/m^{3}catalyst/hr.	250	120	100	100	40	-	-

process in 1941 because the desirability of operating at low temperatures necessitated the use of catalysts which were not qualified for the hot gas recycle process.

The effect of conditions of flow on the reaction, the effect of the large pressure drop across the catalyst bed, and the problem of the energy quantities required will not be discussed here. However, it should be noted that because of the large pressure drop, operation is limited to very thin layers of catalyst, even on a technical scale. Subsequently, Michael turned to experiments on the liquid-phase catalyst suspension process.

b. Synthesis with Catalysts Suspended in a Liquid Medium (Liquid-Phase Catalyst Suspension Process)

Numerous attempts have been made to use catalysts suspended in liquid media for the synthesis. Some of the work has been published:43/

43/ Fischer, F., and Peters, K., Brennstoff Chem., vol. 12, 286, 1931.
Fischer, F., Rolen, O., and Feisst, W., Brennstoff Chem., vol. 13, 461, 1932.
Fischer, F., and Küster, H., Brennstoff Chem., vol. 14, 3, 1933.
Fischer, F., and Pichler, H., Brennstoff Chem., vol. 20, 247, 1939.

Other work at the KWI, the RCh, and the RhPr is still unpublished. In recent years, Michael (I.G.) has studied the problem of catalysts suspended in liquids and named it "liquid-phase catalyst suspension process."

The efficiency of the suspended catalyst is determined essentially by the uniform dispersion of the catalyst and synthesis gas in the oil. According to experiments conducted at the KWI, Mülheim/Ruhr, where such dispersion was to be achieved by suitable stirring arrangement, it it was found that up to a maximum value, the increase in conversion was proportional to the speed of rotation of the stirring device.

In industry, stirring devices of this type give rise to various difficulties. Where such devices are not used, homogeneous suspension of the catalyst in the oil must be controlled by proper gas dispersion and by circulation of the oil, which also removes the heat evolved by the reaction. With a very finely divided catalyst it is easier to maintain a homogeneous suspension than with large particles. Good dispersion of the gas may be attained by bubbling it through porous plates in the bottom of the reaction vessel. The size of the gas bubbles, the optimum height of the liquid column, and the rate at which the gas is bubbled through the porous plate are interrelated. The size of the pores in the porous plates has an important effect on the initial size of the gas bubbles. The behavior of the gas in the reactor is also affected by the pressure, and the entire process is influenced by the viscosity of the gas, which in turn is a function of the temperature. It is advisable to use a high-boiling fraction of hydrocarbon oil from the synthesis as the liquid medium to avoid contamination of the catalyst and products by a foreign substance.

If the operating temperatures are such that the loss of the liquid medium by vaporization or catalytic decomposition does not exceed the production of high-boiling hydrocarbons, the liquid volume is maintained constant by continuous tapping of oil from the reactor. Provision should be made for separating the catalyst from the fraction of the oil that is removed from the apparatus. Fresh catalyst should be added at the same rate that catalyst is removed in order to insure continuous operation.

In the experiments at the KWI, the catalysts for this process were prepared first by thermal decomposition, later by precipitation, and were suspended in high-boiling fractions of synthesis oil. In general, the catalyst was reduced, or pretreated before being introduced into the oil. Michael reported that his iron catalyst was prepared by thermal decomposition of iron carbonyl in oil (250°), or by combustion of iron carbonyl to iron oxide and subsequent reduction (granule size 1 to 5 mm.). The necessary alkali was added to the catalyst as potassium borate (2 percent). Approximately 300 to 400 grams of catalyst and 100 to 200 liters of synthesis gas were used per liter of slurry, making an approximate throughput of 4 liters of gas per 10 grams of catalyst. The pore size of the foam plate averaged between 0.10 and 0.15 millimeters. The synthesis pressure was about 20 atmospheres, and the temperature between 250 and 280°C.

Figure 14b shows a flow diagram of the liquid-phase catalyst suspension process with recycle of a portion of the gas stream.

The fresh gas throughput can be increased with the temperature. At 250°, it should be 80 normal cubic meters per cubic meter of slurry, and at 275°, it should be 125 normal cubic meters per cubic meter of slurry. To keep the rise in temperature between 10° limits, the total quantity of slurry within the converter must be recirculated 20 times per hour. The slurry is cooled in external heat exchangers. To obtain more thorough mixing of oil, catalyst, and gas, gas recycling was introduced. At 250°C. the space-time yield is said to be 0.2 to 0.3 kilograms per liter of converter space per day. Temperatures are about 40°C. higher than with fixed catalyst beds. The maximum allowable temperature is lower because the oil volume decreased by evaporation above 280°C. and would have to be restored by the addition of fresh oil. Since overheating is at a minimum in this process, little methane is produced (usually less than 5 percent).

Table 23 summarizes the data for experiments at 250°C., 280°C., and 300°C. (Michael).

Vertical columns 4, 5, and 6 in Table 22 also summarize experiments with the liquid-phase catalyst suspension process.

To obtain good yields, operation in several stages (3 to 4 stages) with removal of carbon dioxide between stages was found to be advisable.

Table 23. - Comparison of the Products from the Liquid-Phase Catalyst Suspension Process at Different Temperatures

(20 Atm.)

Temp.	250°	280°C.	300°C.
Space-time yield, Kg/liter of catalyst/day	0.2-0.3	0.5-0.6	0.7-0.8
Changes in volume of slurry	Increases	No change	Decreases and must be adjusted
Composition of products, percent			
Gasol	4-6	6	8
Gasoline, -200°C.	30-40	35-50	50-55
Middle oil, -350°C.	32-37	28-33	30-33
Paraffin, above 350°C.	20-30	15-20	5-10
Alcohols in water	6	6	3
Octane number (research) of crude gasoline	50	68	78
Olefin content of middle oil	ca. 60	ca. 60	unknown
Formation of C_1, C_2 (saturated), percent	<5	<5	5

c. Oil Recycle

A possible method of removing the heat of reaction evolved during hydrocarbon synthesis consists in flushing the fixed catalyst bed with oil, which absorbs the heat and is removed from the synthesis apparatus. (A process of this type requires abrasion-proof catalysts.) After external cooling to the desired temperature, the oil is returned to the synthesis apparatus. A portion of the oil is continuously bled off for the recovery of synthesis products. Experiments were carried out by Duftschmitt (I.G. Oppau) among others, who used fused catalysts and stressed the importance of operation at the boiling point of the cooling oil. To avoid recirculating excessive amounts of oil which would introduce a large gas pressure drop, Duftschmitt allowed a temperature differential of 50°C. If the temperature at the entrance to the converter was 240°, it would be 290° at the outlet. At 25 atmospheres pressure, with a carbon monoxide-hydrogen ratio of 1 : 0.82, operation in two stages at this temperature gave 128 grams of liquid hydrocarbons, 22 grams of gasol (C_3+C_4), and 20 to 30 grams of C_1 and C_2 hydrocarbons. A process of this type, if operated at the lowest possible temperatures, would be interesting for catalysts where continuous extraction is desirable (owing to a strong tendency to form high boiling compounds that accumulate on the catalyst). The converters comprised high towers without special internal equipment.

In contrast to the liquid-phase catalyst suspension process, the oil recycle process has the advantage that no special equipment is required for distribution of the gas and for separation of the catalyst.

from the oil. However, the oil must be distributed evenly over the catalyst. Despite the fact that the oil recycle can be kept small and the space-time yields high, better temperature control and product distribution of the liquid vs. gaseous hydrocarbons can be obtained in the liquid-phase catalyst suspension process.

The last two columns in Table 22 summarize experiments based on the oil recycle process of Duftschmitt. The first experiment is an example of hydrocarbon synthesis; the second, at a pressure of 180 atmospheres, a synthesis of considerable amounts of alcohols. Both experiments show that increased pressures result in increased alcohol yields.

If operations were carried out at the boiling point of the cooling oil, this procedure would result in economic difficulties since the cooling oil would be limited to narrow hydrocarbon oil fractions, that would have to be separated from the synthesis products by continuous distillation. Also, the sharp decrease in the partial pressure of carbon monoxide and hydrogen because of the high partial pressure of oil vapor would interfere seriously with the production of maximum carbon monoxide-hydrogen conversion, and with maximum yields.

d. Other Possible Variations

The possible variations in the hydrocarbon synthesis with iron catalysts, discussed in the preceding sections, are not limited to the examples given above. This is explained by the wide range of temperature, pressure, and catalyst composition and preparation possible for operation of iron catalysts in the hydrocarbon synthesis as compared with other hydrogenation catalysts. Similarly, the industrial application can be varied. Operation in stages, hot and cold recycle, fixed and fluidized catalyst beds, direct and indirect removal of heat, etc., can be combined in numerous ways and still further modified when expanded to commercial scale. An interesting example is afforded by the work undertaken in the United States with dry, fixed fluidized catalyst beds, involving an ingenious combination of direct and indirect heat removal. Reports on this process have already appeared in various journals.

PART III

SYNTHESIS OF HYDROCARBONS IN THE PRESENCE OF CATALYSTS BELONGING TO THE PLATINUM GROUP OF THE PERIODIC SYSTEM

1. General Considerations

The use of metals belonging to the platinum group of the periodic system as possible catalysts for the production of hydrocarbons by hydrogenation of carbon monoxide has been the subject of a number of studies.

In 1925, Franz Fischer, H. Tropsch, and P. Dilthey[44] published a paper on "The Reduction of Carbon Monoxide to Methane in the Presence of Different Metals". The experiments, conducted at atmospheric pressure, gave the following sequence for the metals examined as catalysts for the formation of methane:

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[44] Fischer, Franz, Tropsch, H., and Dilthey, P., Brennstoff Chem., vol. 6, 265, 1925.

Ru, Ir, Rh, Ni, Co, Os, Pt, Fe, Mo, Pd, Ag.

Ruthenium heads the list because, as stated in this early report of work at the KWI on the hydrogenation of carbon monoxide, "the commercial powdered metal showed approximately the same degree of activity toward the formation of methane as the current nickel catalyst prepared by special methods". In addition to methane, it was observed that in some instances, small amounts of unsaturated hydrocarbons also were produced for reasons which it was stated, "remained unexplained". Ten years later, Franz Fischer, Th. Bahr, and A. Meusel 45/ published a paper entitled "Catalytic Reduction of Carbon Dioxide to Methane and Higher Hydrocarbons at Atmospheric Pressure". It was found that in the presence of ruthenium, appreciable amounts of carbon dioxide were converted at temperatures as low as 100°, and that in the presence of alkalized ruthenium, other gaseous and liquid hydrocarbons were obtained, probably with the production of carbon monoxide as intermediate. However, in the synthesis of higher hydrocarbons from carbon monoxide and hydrogen the activity of the ruthenium catalyst decreased so rapidly that no quantitative determination was possible. The results obtained for ruthenium could not be reproduced with the other noble metals: rhodium, palladium, platinum, and iridium. As operated, these metals did not reduce carbon dioxide below 400°, with the exception of osmium which reduced carbon dioxide at 200°.

45/ Fischer, Franz, Bahr, ~~Th.~~, and Meusel, A., Brennstoff Chem., vol. 16, 466, 1935.

2. High Pressure Synthesis of Paraffin in the Presence of Ruthenium

In 1938, H. Pichler,[46] reported that a precipitated ruthenium operated at high pressure and a temperature of 200° surpassed all other catalysts for the synthesis of higher hydrocarbons (including cobalt and iron). Maximum yields of higher hydrocarbons were obtained with a uniformity of activity shown by no other catalyst. A large portion of these hydrocarbons comprised previously unknown high molecular weight paraffins, whose melting points ranged to 130° and over. These compounds were pure white, even in the crude state. It was further observed that, in contrast to the early experiments at atmospheric pressure, rhodium and osmium also gave appreciable amounts of liquid and solid products when operated under pressure, although the paraffin yields were smaller than for ruthenium. The extent of carbon monoxide conversion with rhodium was comparable with that of ruthenium. However, in addition to liquid and gaseous hydrocarbons, rhodium produced oxygenated compounds. Osmium showed catalytic activity only above 220°. In this case, also, liquid and solid hydrocarbons were obtained, but as was to be expected at the higher reaction temperature, a considerable quantity of gaseous hydrocarbons were produced. Platinum is much less suitable as a catalyst for the synthesis of higher hydrocarbons. Palladium and iridium gave only traces of reaction products.

A systematic study of the synthesis of paraffins in the presence of ruthenium catalysts at pressures up to 1000 atmospheres was carried

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[46] Pichler, H., Brennstoff Chem., vol. 19, 226, 1938.

out by H. Pichler, and H. Buffleb.[47/]

The reaction proceeds according to the summation equation:

$$x\,CO + 2x\,H_2 \rightarrow x\,CH_2 + x\,H_2O$$

Synthesis gas containing a ratio of 1 CO : 2 H_2 produced yields as high as 190 grams of C_2^+ hydrocarbons (91 percent of the maximum theoretical yield). Solid paraffin represented 64 percent of the total yield (butanone method). A durability test showed that the catalyst could be operated at constant temperature and conversion for more than 6 months (without regeneration, extraction, etc.).

A. The Ruthenium Catalyst

A particularly satisfactory catalyst is prepared as follows: Commercial ruthenium powder is fused with a mixture of potassium hydroxide and potassium nitrate (1 part ruthenium, 10 potassium hydroxide, 1 potassium nitrate) preferably in a silver crucible and stirred with a silver spatula. It is advisable to add the potassium nitrate in small portions. Fusion is complete after 1 to 2 hours. After cooling, the fused mass is dissolved in water; a deep red solution of potassium ruthenate results, which is heated to boiling. Methyl alcohol is added dropwise to the boiling solution. The reduction of potassium ruthenate to ruthenium dioxide begins with the addition of the first drops and goes rapidly to completion. The precipitate settles after a few hours. It is washed on a fritted glass plate, first with water acidified with nitric acid and then

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[47/] Pichler, H., and Buffleb, H., Brennstoff Chem., vol. 21, 257, 273, 285, 1940.

with distilled water. Finally, it is dried at 110°.

Ruthenium differs from the metals of the iron group in that reduction of the dioxide to the metal proceeds just as smoothly at synthesis pressure as at atmospheric pressure. Pure hydrogen can be used. The addition of promoters has no effect on the activity of ruthenium. The same products are obtained in the presence of alkalies or acids. However, the ruthenium catalyst is affected by sulfur compounds and must be operated like the catalysts in the iron group with gases having as low a sulfur content as possible. The catalyst was used initially in a fixed bed in tubes with an inside diameter of 10 millimeters. However, suspensions of ruthenium catalysts in liquid medium have also been used.[48]

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[48] Fischer, Franz, and Pichler, H., Brennstoff Chem., vol. 20, 247, 1939.

B. Effect of Pressure

Figures 15a and b show the effect of pressure on the reaction of carbon monoxide with hydrogen in the presence of the ruthenium catalyst. The logarithms of the pressures are shown on the abscissa. The ordinates in 15a show the carbon monoxide conversion at different temperatures, those of 15b show the carbon balance for experiments conducted at 180°. It will be seen from 15a that at temperatures of 200° or lower, and below 10 atmospheres pressure, no appreciable conversion to higher hydrocarbons can be expected. For this reason, the early experiments at atmospheric pressure had to be operated at temperatures which,

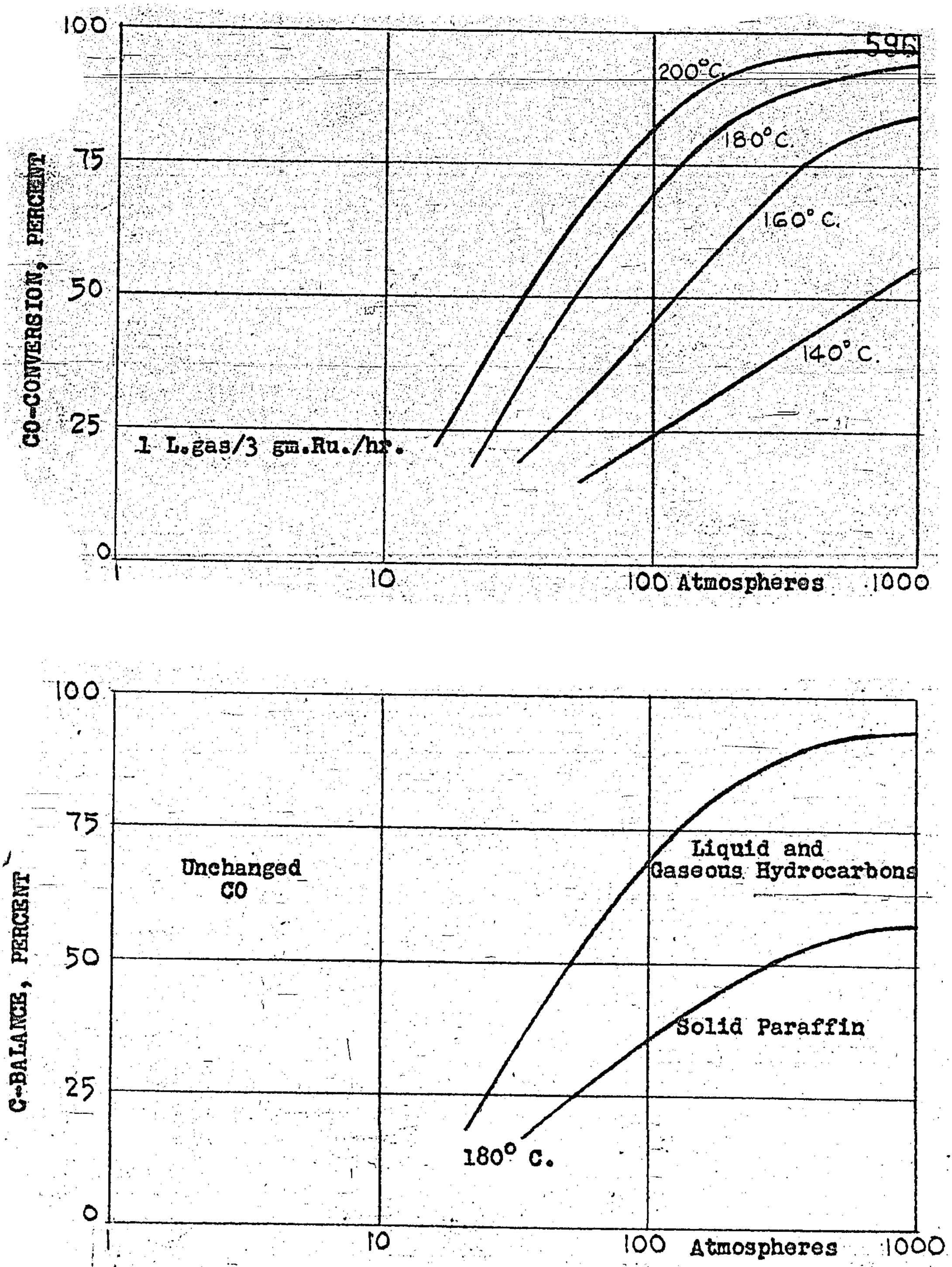

Figure 15: CO-conversion and C-balance at various pressures on a Ruthenium catalyst.

at that pressure, result almost exclusively in the formation of methane.

At 15 atmospheres and 180° the total yield of liquid and solid hydrocarbons was 15 grams per normal cubic meter of ($CO-H_2$) mixture. The carbon monoxide-hydrogen conversion increases with the pressure. At 100 atmospheres and 140°, about 25 percent of the carbon monoxide was converted. At the same pressure and 200°, carbon monoxide conversion was 81 percent. At 1000 atmospheres, the corresponding values were 56 percent for 140°, 94 percent for 180°, and 96 percent for 200°. Yields up to 200 grams per N cubic meter were obtained. Figure 15b shows the distribution of the products obtained from a series of experiments at 180°. At 1000 atmospheres, 57 percent of the carbon monoxide charged to converter or 61 percent of the carbon monoxide converted, and 71 percent of the solid and liquid product was obtained as solid paraffin having a pure white appearance in the crude state. At lower temperatures the paraffin fraction exceeded 80 percent.

Since ruthenium is not as sensitive to temperature as the catalysts of the iron group, and approximately the same yields of solid and liquid hydrocarbons may be obtained for the range from 190 to 240°, conversion is approximately the same at 100 atmospheres and higher temperatures as at 1000 atmospheres and correspondingly lower temperatures. Above 300°, conversion between 100 and 1000 atmospheres also results in the formation of methane and carbon dioxide.

Space-Time Yields from Ruthenium Catalysts.

In figure 16 are plotted the gas throughput (liters per gram of ruthenium per hour) as abscissas, the yields in grams per normal cubic meter of (CO-H2) mixture on the left ordinates, and the space-time yields in grams per kilogram of ruthenium per hour on the right ordinates. Experiments are based on a pressure of 100 atmospheres. The yields per normal cubic meter of gas (curve 1) drop off from 188 - 190 grams at a gas throughput of 1 (liter of synthesis gas per gram of ruthenium per hour) to 119 grams at a throughput of 5 liters per hour and to 62 grams at a space velocity of 10 liters per hour. Under the same conditions, the space-time yields (curve 2) rise from 38 grams per kilogram of ruthenium per hour, at a gas throughput of 1 liter per gram of ruthenium per hour, to 118 grams for 5 liters per hour and 164 grams for 10 liters per hour. The maximum is reached at 168 grams at 12 liters per hour.

Whereas the yields based on the gas throughput increase as the throughput decreases (approaching maximum theoretical yields for very small throughputs) the space-time yields increase with increasing gas throughput to a maximum and then decrease. When operating in the neighborhood of this maximum, if extensive conversion is required, multistage operation is recommended. In general, the curves shown in figure 16 are typical of all other catalysts.

Given ruthenium catalyst pellets weighing 1 gram per cubic centimeter and the appropriate synthesis apparatus, the maximum of curve 2 (based on the catalyst volume) would correspond to a space-time

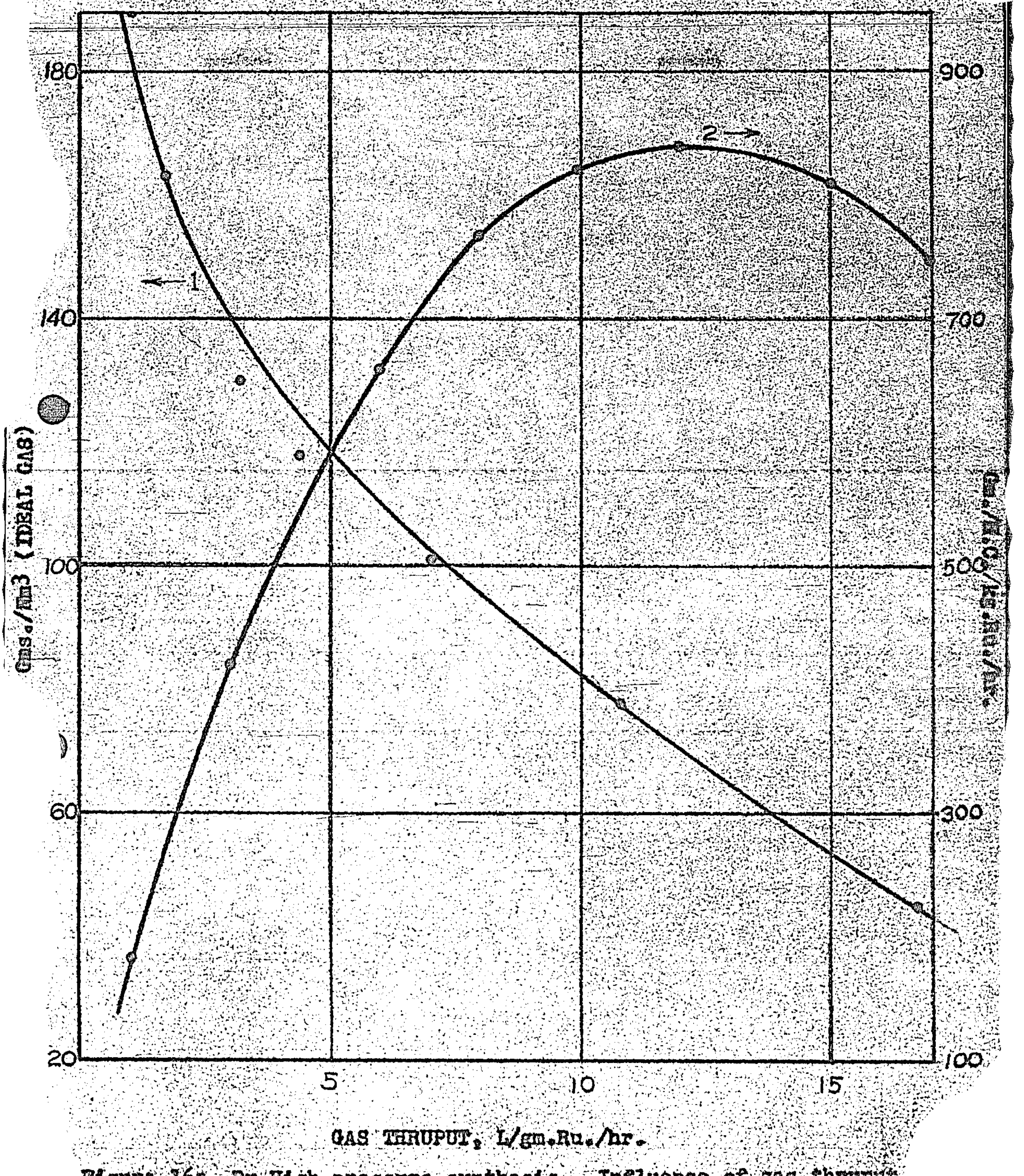

Figure 16: Ru-High pressure synthesis. Influence of gas thruput on yields.

yield 100 times that which is now obtained industrially with cobalt catalysts. The cost of ruthenium constitutes an obstacle to its use on an industrial scale. This situation might be altered, at least to some extent, if some use could be found for the hitherto unknown high molecular weight paraffins produced by the synthesis over ruthenium catalysts.

D. Ruthenium Paraffins

The total crude, snow white reaction product from a 100-atmospheres operation collected from the receiver of the synthesis apparatus by heating to about 150°, melted sharply at 114°. The oil-free paraffin content, determined by the butanone method, amounted to 70 to 80 percent (equivalent to 60 to 70 percent based on the total quantity of liquid and solid hydrocarbons, including gasoline recovered from activated charcoal trap). The total paraffin recovered from the liquid fractions with butanone had a final melting point of 118 to 119°.

The product was fractionated by extraction with cold and boiling benzene. Thirteen percent of the oil-free paraffin was virtually insoluble in boiling benzene and melted between 126 and 128°C. Fifty-three percent dissolved in boiling benzene, but was insoluble in cold benzene and had a final melting point of 113°. Extraction of the catalyst with boiling toluol produced paraffins melting up to 132°. Elementary analysis of the different paraffin waxes gave the following data: 85.4 to 85.5 percent of carbon and 14.2 to 14.5 percent of hydrogen.

Fractional extraction at different temperatures of a ruthenium paraffin obtained at 1000 atmospheres resulted in the fractions tabulated in table 24. The product was separated into 5 fractions. About a third of the product had an average melting range of 51° to 57°C., 14 to 17 percent melted between 92.5° and 95°, and approximately half melted above 120° and corresponded to a product not previously reported by other workers.* The densities of the paraffin fractions at 20° ranged up to 0.785. It will be seen from the last three columns of the table that the viscosity of the melted paraffins increases appreciably with the molecular weight. The highest molecular weight paraffins in the fused state are extremely viscous substances. Figure 17 shows the rise in the average melting point with the increase in the number of carbons per molecule for known paraffins. The new paraffins lie on the same continuous curve predicted from the curve for the known paraffins. For the highest molecular weights the melting points converge around 134 to 135°C. The two other curves represent the viscosity of the paraffins in centistokes at 150° and 180°, respectively. The viscosity of the melted paraffins is a function of their molecular size.

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* Difficulties were encountered in determining the average molecular weight of the highest molecular-weight paraffins because of their low solubility and because of their slight effect in increasing the boiling point or depressing the freezing point of solvents. Best results were obtained by determining the increase in the boiling point of pure toluol (differential measurements for the elimination of variations in pressure). The method proposed by Staudinger, [Kolloid Z., vol. 51, 71, 1920], for the determination of the viscosity of dilute solutions cannot be used owing to the insolubility of the products at room temperature.

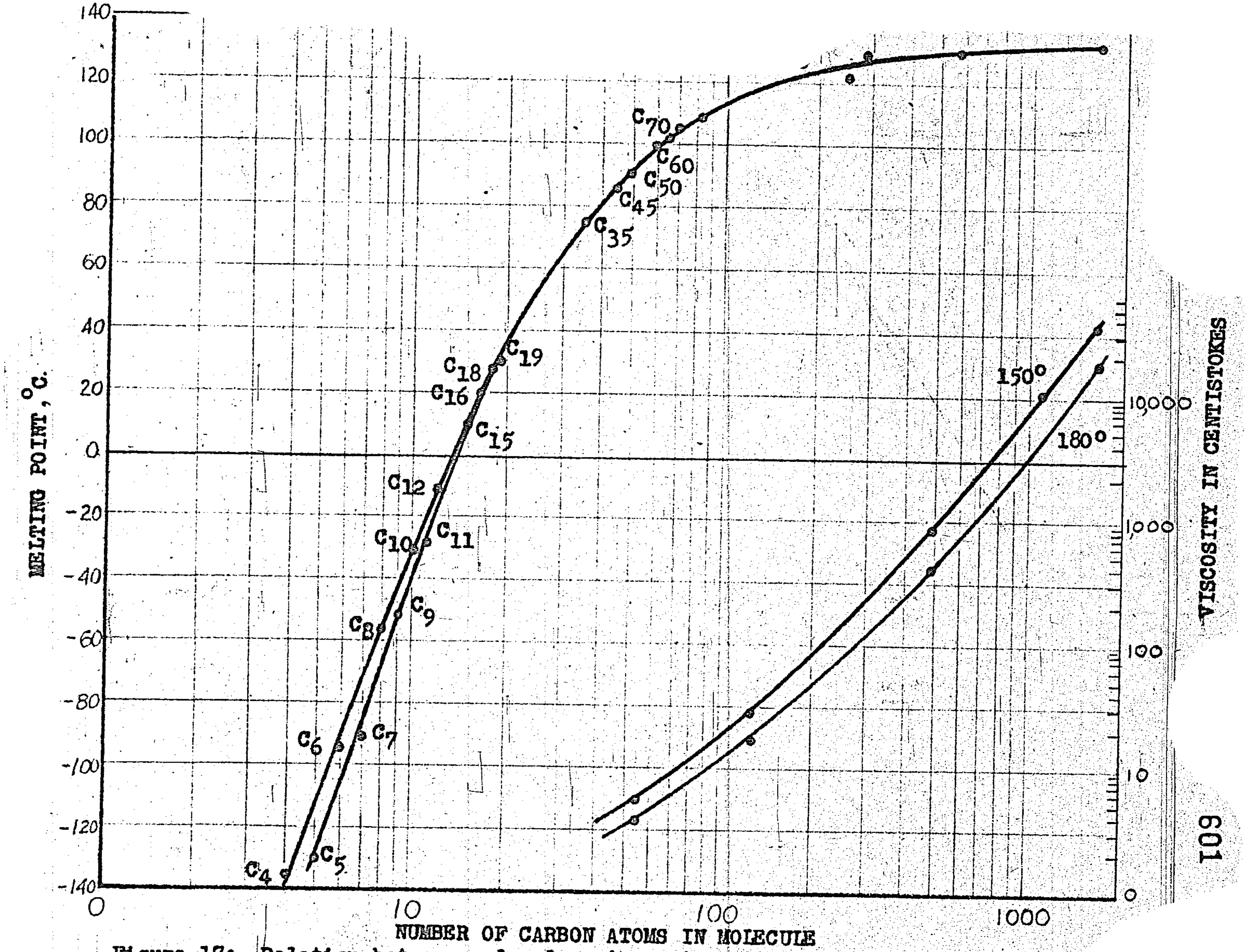

Figure 17: Relation between molecular size, viscosity and melting point of paraffins.

Table 26. – Some Extraction Data for Ruthenium Paraffins

Fraction	Solvent	Extraction Temp. °C.	Amount Dissolved (per cent of crude product)	Boiling Range °C.	Density 20°	Density 130°	Average Mol. Wght.	Viscosity Centistokes 150°	Viscosity Centistokes 180°	Viscosity Pole Height V_p
1	n-pentane	34	30-33	51-57	-	-	-	-	-	-
2	n-hexane	68	14-17	92.5-95	-	0.7654	760	6.06	4.0	1.2
3	Kogasin fraction	90	14-16	121-122.5	0.966	0.7779	1750	28.6	18.6	1.2
4	n-heptane	98	20-25	129.5-130.4	0.978	0.7827	6800	670	110	1.2
5	Kogasin fraction	121	12-15	132-134	0.980	0.7859	23000	39600	15800	1.4

PART IV

SYNTHESIS OF HYDROCARBONS IN THE PRESENCE OF OXIDE CATALYSTS

1. Isosynthesis

Iso-paraffins are of particular interest as motor fuel. Their high anti-knock properties, good lead susceptibility, and thermal behavior make them superior as motor fuel to other types of hydrocarbons. Comparison of saturated hydrocarbons which are favored as high efficiency fuels shows that the anti-knock rating, which is so important in this respect and is generally expressed as the octane number, increases with the compactness of the paraffin molecule and is particularly high when tertiary, or preferably quaternary, carbon atoms are present.

It is well known that at present iso-paraffins are produced chiefly by polymerization of olefins by alkylation (such as the reaction of iso-butane with n-butene) or by isomerization of appropriate n-paraffin hydrocarbons.

H. Koch, and F. Hilberath,[49] undertook a detailed study of the nature of the low-boiling (below 100°C.) hydrocarbons obtained in the Fischer-Tropsch synthesis over cobalt catalysts. Of the saturated hydrocarbons, 7.5 percent of iso-butane was found in the C_4 fraction. In addition to the predominant n-paraffins, n-pentane, n-hexane, and n-heptane, precise distillation of the C_5 fraction showed the presence of

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[49] Koch, H., and Hilberath, F., Brennstoff Chem., vol. 22, 135, 145, 1941.

small-chain branched hydrocarbons, such as methylbutane, 2-methylpentane, 3-methylpentane, 2-methylhexane, and 3-methylhexane. Multiple branched chains were present, if at all, only in traces. As to the extent of branched-chain hydrocarbon formation in the Fischer-Tropsch Synthesis, von Weber[50] reports that for the hexane fraction the degree of branching (mole fraction containing branched chains) is 0.15, 0.20 for heptanes, 0.27 for octanes, 0.35 for nonanes, and 0.40 for decanes. It seems, therefore, that for the region examined the synthesis gives rise to one tertiary carbon atom out of 25 to 50 carbons with no evidence of any quaternary carbon atoms. Similar results were obtained from the examination of the degree of branched-chain ~~formation in the~~ hydrocarbons produced by medium-pressure synthesis with iron catalysts (see products, Schwarzheide experiments). Eleven to 16 percent of the C_6 fraction and 11 to 18 percent of the C_7 fraction were composed of simple branched-chain hydrocarbons. The predominance of n-paraffins, or n-olefins, is characteristic of the hydrocarbons obtained with catalysts of the iron group catalysts and with ruthenium.

One possible method for the synthesis of iso-paraffins from carbon monoxide and hydrogen consists in the preparation of iso-butyl alcohol in the presence of alkalised zinc catalysts (see part I, Methanol Process), followed by dehydration of the alcohol to iso-butene,

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[50] von Weber, Angew. Chem., vol. 52, 607, 1939.

from which higher branched hydrocarbons may then be obtained by standard procedures. However, since methanol is the chief product formed in the iso-butyl alcohol process, this method offers only a partial solution to the problem of a procedure for synthesising branched-chain paraffin hydrocarbons. (Hydrogenation of coal at high pressure by the Bergius-I.G. process, gives principally naphthenic and aromatic hydrocarbons.)

A process for the direct preparation of iso-paraffins as the principal products, based on water gas prepared from coal or natural gas, was not known previously. The problem of a process of this type is discussed in the following pages. The result is a new synthesis to which the name of "iso-synthesis" has been given. As in the synthesis of n-paraffins, the starting materials are carbon monoxide and hydrogen. However, in contrast to the hydrocarbon synthesis already described, the catalysts are oxides, particularly thorium oxide. The temperature required are considerably higher than those in the n-paraffin synthesis.

A. The Catalyst

When water gas is passed through an empty steel tube, for instance, at a pressure of 30 atmospheres and a temperature of 450°, the carbon monoxide and hydrogen react to give chiefly carbon, carbon dioxide, and low molecular-weight hydrocarbons, especially methane. The results of low temperature distillation of the C_3-C_4 fraction produced distillation curve I represented in figure 18. No characteristic break was observed at the boiling point of iso-butane (-11.8°C.). In addition to n-butane and n-butene, small amounts of iso-butene were present in the fraction

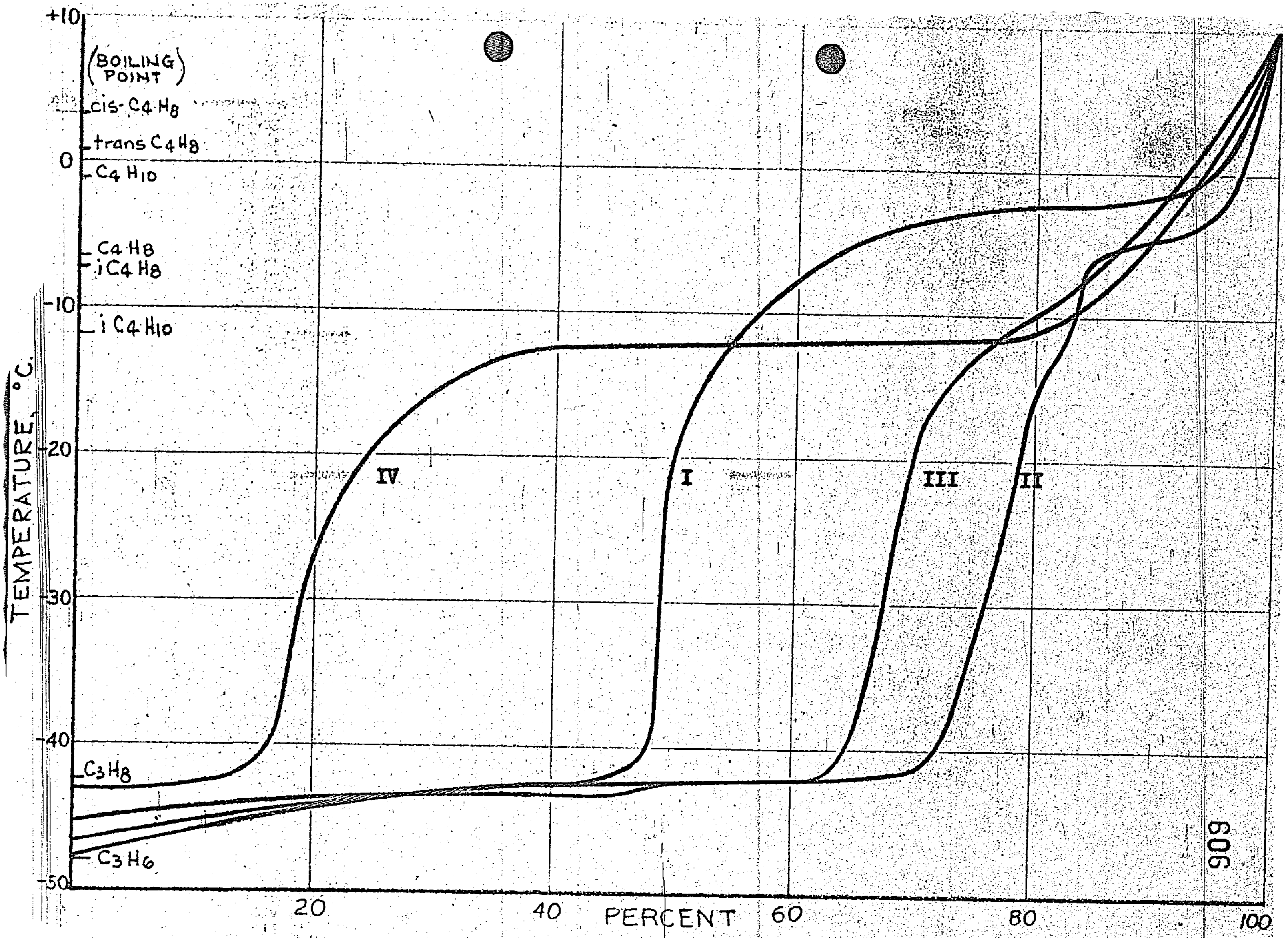

Figure 18: Low temperature distillation of C_3-C_4 fractions from different catalysts.

that distilled between -10 and 0°C. (iso-butene was removed with 64 percent concentration of sulfuric acid and its presence was also determined with mercuric nitrate).

The use of active catalysts belonging to the iron group of the periodic system produces good yields of predominantly straight-chain hydrocarbons at temperatures between 180 and 300°C. At higher temperatures, the principal products are carbon and methane. Catalysts of this type are not suitable for the iso-synthesis.

When, for instance, carbon monoxide and hydrogen are treated at 400° to 450°C. in a copper-lined reaction tube in the presence of methanol catalyst, small amounts of hydrocarbons form in addition to oxygenated compounds. Curve II, figure 18, shows the distillation curve for the C_3-C_4 fraction obtained with a zinc-copper catalyst. No appreciable formation of iso-butane was observed; the iso-butene content was 0.2 gram per normal cubic meter of synthesis gas.

Curve III represents the distillation curve for the C_3-C_4 fraction of a hydrocarbon mixture obtained with a precipitated aluminum oxide catalyst (operation with water gas as the synthesis gas, 150 atmospheres, 450°). The portion of the curve corresponding to the fraction that distills between -15 and -5°C., indicates the presence of iso-butane. However, the quantity was very small.

Completely different results were obtained when thorium oxide was used as catalyst. Curve IV shows that with this catalyst iso-butane, b.p. -11.8°C., represents one of the principal products. This new observation constitutes the basis of the iso-synthesis. In addition to iso-butane, Other liquid branched-chain hydrocarbons are also produced and virtually no straight-chain products.

In general, the thorium catalysts were prepared by precipitation with sodium carbonate. The catalysts were pretreated by sintering in a stream of air at 400°C. The [illegible] is [illegible], particularly when regenerated with air periodically (depending on the conditions, every few weeks) was found to be of considerable benefit. Thorium oxide is not affected by sulfur compounds. On a single pass over the catalyst (no recycling) carbon monoxide and hydrogen are used up in a ratio of 1.2 CO to 1 H_2. It is important that the synthesis be carried out in converters whose walls are inert under the conditions of the synthesis. The iso-synthesis experiments were carried out either in chrome alloy steel tubes or in steel tubes lined with copper.

A large number of unpromoted oxides was studied to determine their activity as catalysts for the reaction between carbon monoxide and hydrogen. The oxides of thorium, aluminum, chromium, titanium, beryllium, zirconium, uranium, zinc, manganese, magnesium, cerium, and lanthanum were investigated. Of these, thorium oxide, zirconium oxide, and to a small extent, cerium oxide, were active as catalysts for the iso-synthesis. Iso-hydrocarbons were produced in the presence of aluminum oxide, but the reaction was accompanied by the production of considerable amounts of methane and carbon. Table 25 summarizes data for the behavior of ThO_2, ZrO_2, CeO_2, and Al_2O_3 used as unpromoted catalysts. Operation was carried out at 450°C. and 150 atmospheres. In addition to the amount of carbon monoxide conversion, the extent of iso-butane formation is shown as a criterion of the activity of the catalyst for the iso-synthesis.

Table 40. - Behavior of Various Unpromoted Catalysts in the Iso-Synthesis, Particularly with Respect to Iso-C_4-Hydrocarbons

Catalyst	Conversion, volume percent	Iso-C_4, g/Nm³ $(CO+H_2)$	Percent of iso in C_4 fraction	Liquid Products g/Nm³ $(CO+H_2)$
ThO_2	46	10	86	40
ZrO_2	[illegible]	9	82	[illegible]
CeO_2	10	1.3	81	[illegible]
Al_2O_3	55	2.8	59	5

Thorium oxide gave a conversion of 46 volume percent of the carbon monoxide-hydrogen mixture. The yield of iso-butane was 10 grams per normal cubic meter of $(CO+H_2)$. Of the total C_4 fraction, 86 percent consisted of iso-C_4-hydrocarbons. In addition, 40 grams of liquid hydrocarbons was obtained. With zirconium oxide, a 30-percent conversion of carbon monoxide-hydrogen mixture was obtained and 9 grams of iso-C_4 hydrocarbons. Here too, 82 percent of the C_4-fraction consisted of iso-hydrocarbons. Cerium oxide produced a much smaller degree of conversion. Aluminum oxide, prepared from sodium aluminate, proved to be very active as a catalyst for the conversion of carbon monoxide and hydrogen, but the quantity of iso-C_4-hydrocarbons and liquid products was small.

When unpromoted, the remaining oxides investigated, as well as preparations of aluminum oxide obtained by widely differing procedures, either showed small carbon monoxide-hydrogen conversion, or chiefly methane and carbon.

B. Effect of Reaction Temperature

Single-Component Catalyst

Figure 19 shows diagrammatically the type of products formed in the iso-synthesis as a function of temperature over thorium oxide, at an operating pressure of water gas of 150 atmospheres. Operating temperatures are shown on the abscissa and the average composition of the product (percent) on the ordinates.

It will be seen from figure 19 that below the temperature region suitable for the iso-synthesis, for example, at temperatures below 400°, particularly below 375°, alcohol formation is preponderant, whereas above 475°, particularly above 500°, the formation of undesirable gaseous hydrocarbons, such as methane, ethane, and propane predominates. Between these two limits lies the temperature range of the iso-synthesis. At 450°C., a temperature at which formation of oxygenated compounds is small, the products obtained consist of 15 percent of methane and a few C_2-hydrocarbons, 13 percent of C_3 and n-C_4 hydrocarbons, principally propane, 26 percent of iso-C_4 hydrocarbons, principally iso-butane, and 46 percent of liquid products, containing chiefly branched aliphatic hydrocarbons, together with some napthenes and aromatics.

C. Effect of Pressure (ThO_2 Single-Component Catalyst)

Figure 20 shows the results obtained from experiments conducted at varying pressures. Yields are based on 1 normal cubic meter of carbon monoxide-hydrogen mixture. Operation was conducted in each case with 10 liters of end gas per hour per 28 grams of ThO_2. The temperature was maintained at 450°C. throughout.

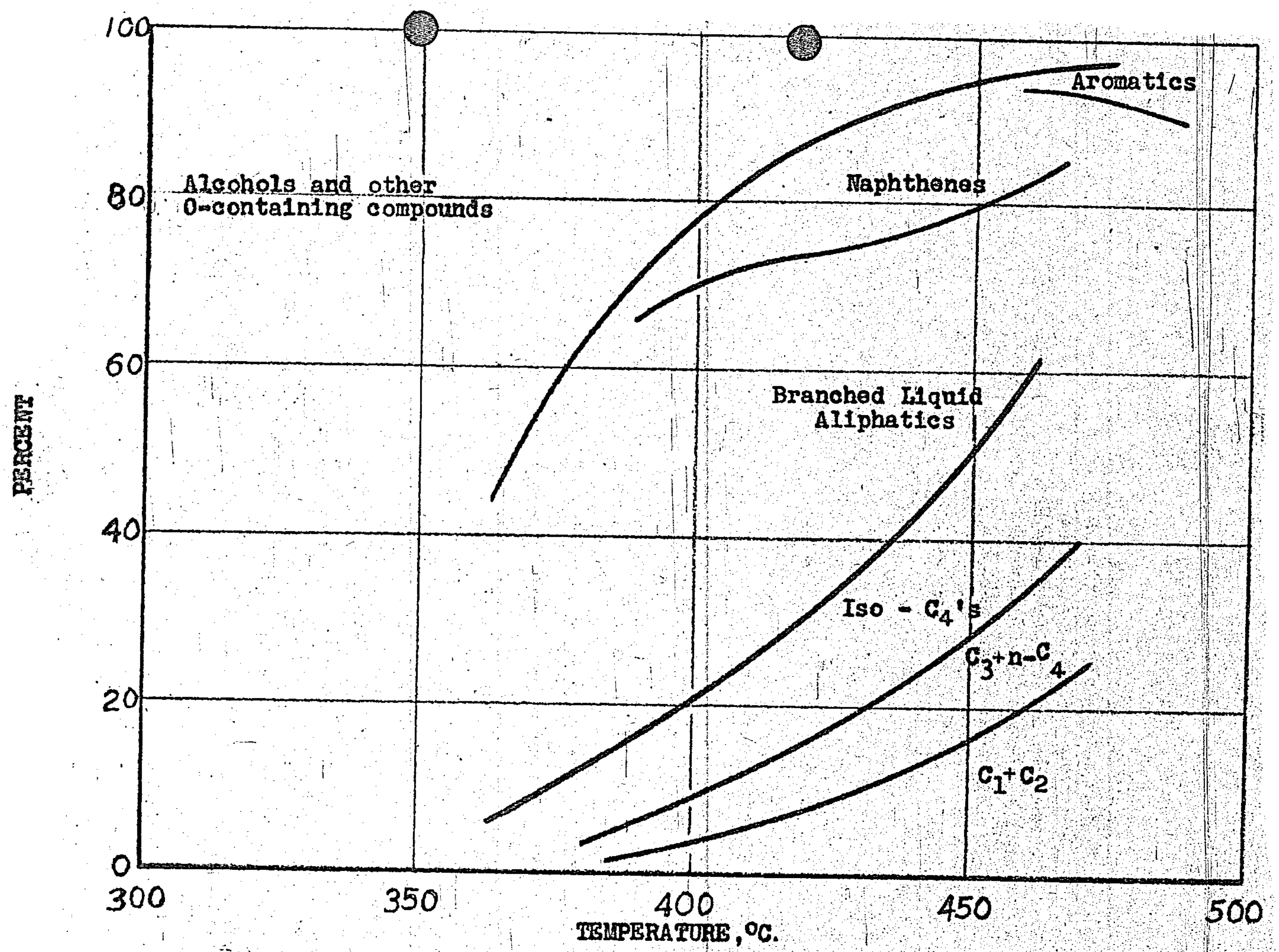

Figure 19: Reaction product composition as related to temperature. (ThO_2 single component catalysts)

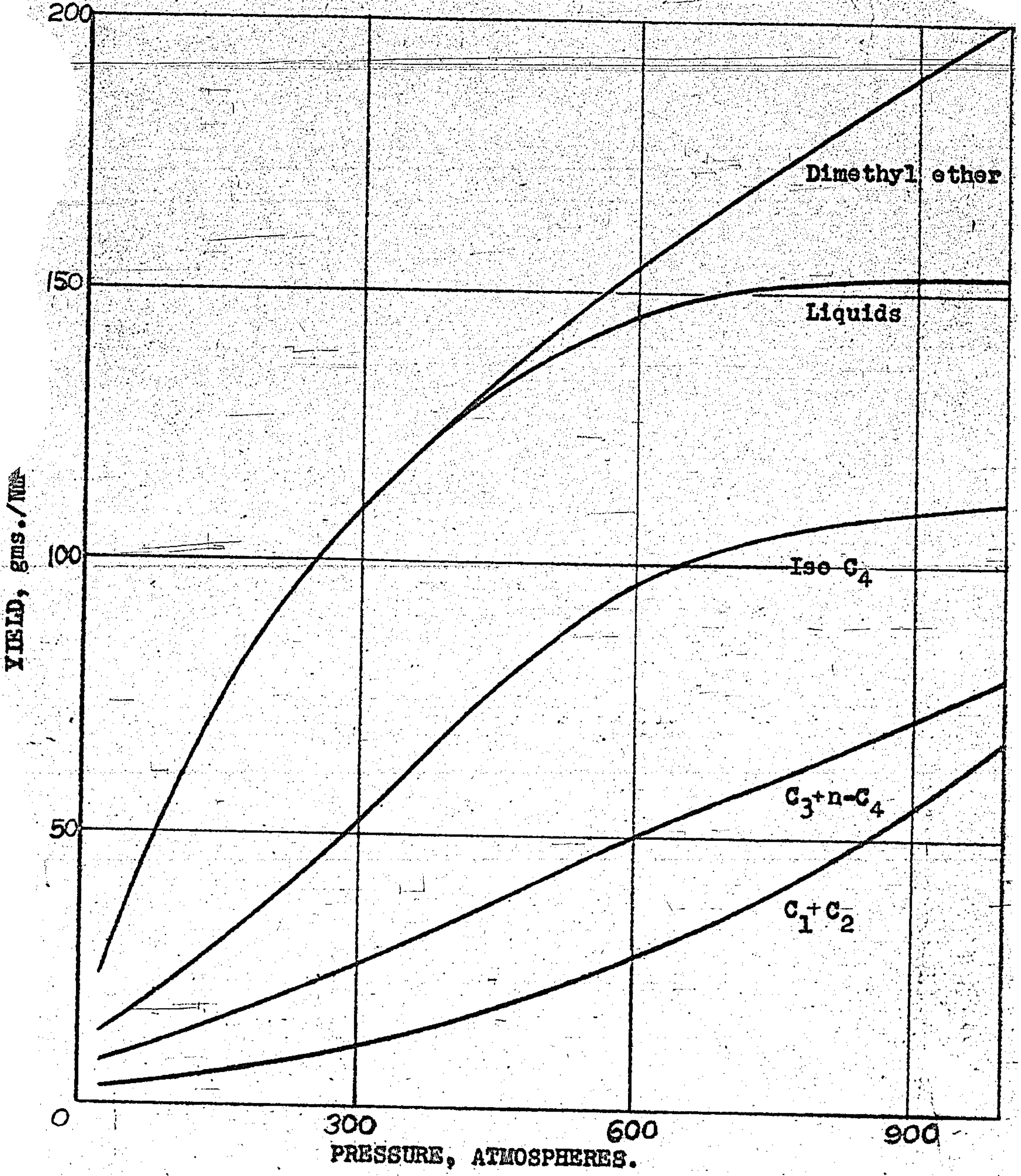

Figure 20: Influence of pressure on the amount and kind of products from the Iso-Synthesis. (ThO_2 single component catalysts, 450°C.)

At atmospheric pressure, conversion of the synthesis gas was small, generally less than 3 percent. It will be seen from figure 20 that optimum conditions for production of gasol and liquid hydrocarbons prevail at pressures between 300 and 600 atmospheres. At lower pressures carbon monoxide-hydrogen conversion was unsatisfactory; at higher pressures the formation of methane and dimethyl ether predominated. Pressures of 1000 atmospheres and higher were too high for the thorium oxide single-component catalyst, even at temperatures other than those used in the experiments shown. For pressures of this order, temperatures below 450° produced increasingly large amounts of dimethyl ether (400°, 1000 atm., 200 g dimethyl ether per Nm^3), whereas temperatures over 450° resulted in increased methane production. With increasing pressure and temperature, the yields obtainable per unit volume of synthesis gas in a single stage increase. With increasing temperature, the range in which oxygenated compounds form in considerable amounts becomes smaller but there is still no appreciable methane formation.

Increased synthesis gas pressure is accompanied by an increase in gas conversion, which is too high to be explained on the basis of increased contact time in the converter. Thus, at 600 atmospheres the space-time yield was 8 times higher than at 150 atmospheres.

D. Experiments with Multi-Component Catalysts

The following combinations were among the multi-component catalysts investigated:

The effect on the action of ThO_2 catalyst of small amounts of alkali will be seen from table 26. The presence of alkali lowers the activity of the catalyst in much the same way as it reduces the activity of catalysts of the iron group. For small amounts of alkali (less than 1 percent) and at constant carbon monoxide conversion, a decrease in the production of gaseous products is noticeable. The presence of alkali makes it possible to carry out the synthesis at relatively high temperatures, without converting a considerable portion of the carbon monoxide-hydrogen mixture to methane. This means that operation may be conducted over a temperature range resulting principally in the formation

Table 26. - Synthesis in the Presence of a ThO_2 Catalyst Containing a Small Amount of Alkali

(0.6% K_2CO_3, 300 Atm., 450°, 10 Lit. End Gas/28 g ThO_2/Hour

		Yields (g/Nm^3 $CO-H_2$ mixture)							
			Alcohols in						
K_2CO_3 Percent	CO Conversion Volume Percent	Liquid Hydrocarbons	Oil	H_2O	i-C_4	n-C_4	C_3	C_2	C_1
0	62	42	9	11	23	3	11	4	11
0.6	62	65	21	5	12	1	8	1	6

of cyclic hydrocarbons. Thus, at 30 atmospheres and 500°, a thorium oxide catalyst containing 1 percent of potassium carbonate produced a liquid hydrocarbon fraction of which 42 percent was napthenic and 8 percent aromatic, the latter consisting chiefly of toluene and containing 3 percent of phenols.

For experiments in an acid medium, a precipitated thorium oxide preparation was dried at 300°, pulverized, and made into a paste with phosphoric acid, which was dried at 250°. A catalyst of this type produced a decrease in carbon monoxide-hydrogen conversion and in the yields of liquid hydrocarbons, and an increase in the formation of methane. Thorium phosphate showed no catalytic activity.

Aluminum oxide is not suitable as a single-component catalyst for the synthesis of iso-hydrocarbons, but when added to thorium oxide its effect on the activity of that compound is striking. A considerable increase in iso-C_4 yields was obtained with $ThO_2-Al_2O_3$ catalysts. Experiments in which 20 percent of aluminum oxide was added to thorium oxide

CO Conver-
sion Volume
Percent

same amount of alkali (0.6 percent, K_2CO_3, based on ThO_2) was added to the thorium precipitate before mixing with the aluminum compound, the promoting action of aluminum oxide diminished.

The presence of zinc oxide in thorium catalysts increased the amount of liquid products. There was no tendency towards carbon formation.

In contrast to thorium oxide, aluminum oxide and zinc oxide proved unsuitable as single component catalysts for the isosynthesis. When added to the thorium oxide, aluminum oxide increased the formation of iso-butane, and zinc oxide increased formation of liquid products. The search for a possible substitute for thorium oxide led to the discovery that a two-component catalyst, composed of aluminum and zinc oxides, was capable of catalyzing the formation of higher hydrocarbons as well as that of iso-butane. However, the space-time yields obtained with catalysts of this type are lower than those given by the corresponding ThO_2 catalysts.

Three-component catalysts, thorium, zinc, and aluminum oxides, gave results similar to those obtained with ThO_2-ZnO catalysts (in the absence of Al_2O_3).

Aluminum and chromium oxides used as two-component catalysts showed little activity. However, it is interesting to note that catalysts of this type, operated at 500°, produced liquid hydrocarbons composed almost exclusively of aromatics. Figure 21 shows a distillation curve of the liquid products obtained with these catalysts. The points characteristic of benzene, toluene, and xylene are present. There is also some indication of the presence of mesitylene. The individual fractions had the following refractive indices:

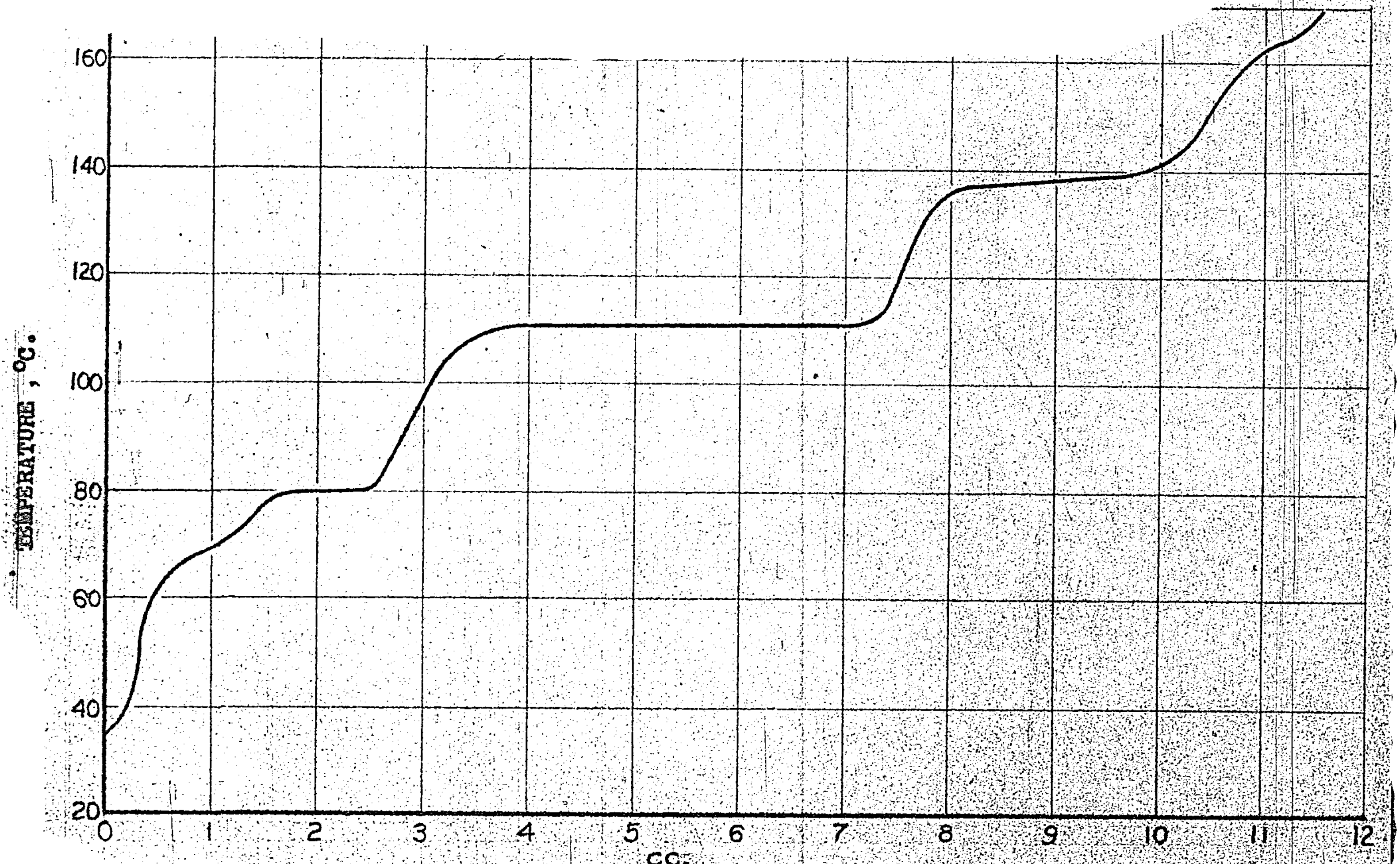

Figure 21: Boiling curve of liquid reaction products from Al_2O_3+10 percent Cr_2O_3 experiment.

boiling range of fraction, °C.	refractive index n_D^{20}
below 79	1.4090
79-83	1.4795
83-109	1.4619
109-113	1.4929
113-137	1.489
137-147	1.4960
over 147	1.4994

As compared with thorium oxide catalysts containing no chromium, thorium oxide-chromium oxide catalysts gave increased yields of iso-butane, but as compared with thorium oxide-aluminum oxide catalysts these yields were considerably lower.

Addition of iron to the thorium oxide catalyst, even in very small amounts, increased methane formation. Consequently, care should be taken that the synthesis gas introduced into the converter contains no iron carbonyl, which decomposes at the temperature of the iso-synthesis.

The copper lining of the reaction tubes does not participate in the synthesis, but the addition of copper by simultaneous precipitation with thorium oxide, increased the formation of gaseous and aqueous products, as well as that of carbon.

Addition of kieselguhr to an active thorium oxide-aluminum oxide catalyst resulted in a marked increase in the production of methane and of higher molecular weight-straight chain homologues of methane (C_4 fraction : 33% n-C_4, as against 13% with catalysts containing no kieselguhr).

E. The Liquid Reaction Products

In thq preceding sections it was shown that the nature of the products obtained by iso-synthesis is determined essentially by the type of catalyst, the reaction temperature, and the synthesis pressure. At low temperatures and high pressures, the tendency is towards alcohol formation. The alcohol fraction in the water obtained as by-product consists mainly of methanol in the oil fraction, principally iso-butyl alcohol. At higher temperatures, in addition to saturated and unsaturated aliphatic hydrocarbons, napthenes and aromatics are produced in increasingly large amounts.

The boiling range of products from low-temperature operation is higher than from high-temperature operation. Before investigation of the hydrocarbons, alcohols were removed by washing with water and brine and finally by treatment with sodium. The unsaturated and aromatic content of the liquid hydrocarbons increased with increase in boiling range of the product. An experiment conducted with a thorium oxide + 20% aluminum oxide catalyst at 300 atmospheres and 425°C. gave a product which contained 25 percent of unsaturated and 0% of aromatic hydrocarbons in the 65-95°-fraction, and 62 percent of unsaturated and 31 percent of aromatic components in the 175-195°-fraction. With lower reaction temperature, the unsaturated fraction of the liquid hydrocarbons is larger and the aromatic fraction smaller.

Precise distillation was carried out for the purpose of identifying the hydrocarbons obtained by iso-synthesis. After removal of the alcohols, the hydrocarbons were hydrogenated in the presence of nickel catalysts at the lowest possible temperatures and the highest possible hydrogen pressures, and then dried over sodium. Figure 22 shows the results of a distillation on the product obtained by this treatment (1-meter spinning band column). Curve 1 is the distillation curve; curve 2 shows refractive indices; and curve 3, aniline points. Portions of the fractions were subjected to a second precise distillation.

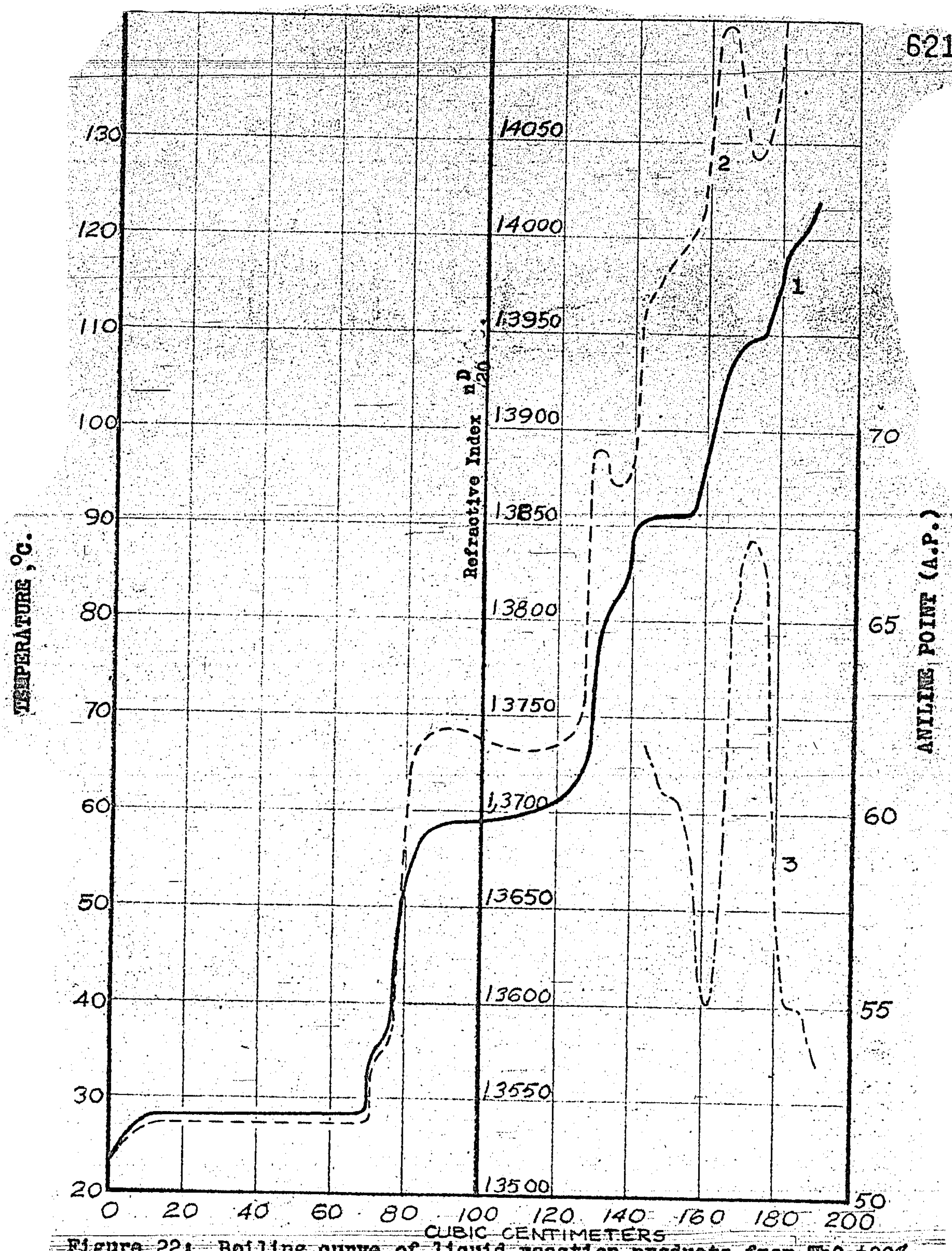

Figure 22: Boiling curve of liquid reaction products from ThO_2+20% Al_2O_3 Experiment (250a)

The product examined contained the following fractions:

	Percent
C_5 - paraffin hydrocarbons	34
C_6 - paraffin hydrocarbons	21
C_7 - paraffin hydrocarbons	10
C_8 - paraffin hydrocarbons	5
napthenes	19
higher hydrocarbons	11

The C_5 and C_6 fractions had the following composition:

C_5 Fraction	Percent
2-methylbutane	91
n-pentane	9
C_6 Fraction	
2,2-dimethylbutane	3
2,3-dimethylbutane	47
2-methylpentane	31
3-methylpentane	16
methylcyclopentane	3
n-hexane	traces

In the crude state, the liquid hydrocarbons from isosynthesis have an octane number (motor method) of approximately 80. By mixing with the gasoline obtained from alkylation of the iso-butane which constitutes the main product of isosynthesis, and addition of lead tetraethyl, the octane number rises to 100.

PART V
BRIEF CONSIDERATIONS ON THE MECHANISM OF THE HYDROGENATION OXIDES OF CARBON

It has been customary in the past to distinguish between two fundamentally different types of hydrogenation of carbon monoxide. In one case, metallic catalysts with strong hydrogenating capacity produce methane and predominantly straight chain homologues of methane; in the other, oxygenated compounds are produced in the presence of oxide catalysts. In each of these two reaction groups are included a number of different syntheses. Thus, the first group includes a synthesis by which methane exclusively is formed, another which produces principally liquid hydrocarbons, and still others resulting chiefly in solid paraffins. In the second group we may distinguish a specific synthesis for methanol, an iso-butyl alcohol synthesis (in which 20% iso-butyl alcohol forms, in addition to methanol), and a synthesis giving a mixture of very different alcohols, aldehydes, ketones, and acids (synthol). It was assumed that the two syntheses in which not only the catalysts but other operating conditions differed, proceeded along fundamentally different paths. Nevertheless, some divergence of opinion existed and it was suggested that hydrocarbons might be formed by way of intermediate oxygenated organic compounds.

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[51] Elvins and Nash, Fuel, vol. 5, 263, 1926.

[52] Elvins, Jour. Soc. Chem. Ind., vol. 46, 473 T, 1927.

[53] Smith, Hawk, and Golden, Jour. Amer. Chem. Soc., vol. 52, 3221 ~~[illegible]~~, 1930.

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1. Early Views on the Course of the Hydrocarbon Synthesis, Particularly in Normal Pressure Reactors

In the synthesis of higher hydrocarbons in the presence of catalysts of the iron group catalysts, Franz Fischer and his collaborators postulated the intermediate formation of carbides. Methane formation may proceed by a different path, such as the formation of intermediate compounds between the metal and hydrogen. These assumptions were based on the following observations:

1. Catalysts of the iron group used in synthesizing higher hydrocarbons always contain carbides.

2. Those carbides can be converted to higher aliphatic hydrocarbons by treatment with acids.

3. Except in such cases where carbon monoxide can be shown to form as an intermediate in the presence of synthesis catalysts, mixtures of carbon dioxide and hydrogen always produce methane, but no higher hydrocarbons.

The presence of carbon monoxide on the catalyst surface and possibly also the reactions that accompany the formation of higher hydrocarbons, appear to impede the formation of the hypothetical metal-hydrogen compounds, (assumed to be intermediate in the production of methane) since there is no reaction between carbon dioxide and hydrogen as long as carbon monoxide is present in appreciable amounts in mixtures of carbon monoxide, carbon dioxide, and hydrogen.

The theories relative to the chemical processes accompanying the Fischer-Tropsch synthesis, by Franz Fischer and his collaborators, were formulated as follows in 1932:

"Carbon monoxide and hydrogen are first adsorbed on the catalyst surface. The carbon monoxide then undergoes chemical fixation at the active centers with loosening of the carbon-oxygen bond. Hydrogen, or excess carbon monoxide on the iron, reacts with the oxygen to water, or carbon dioxide, respectively. The carbon, bound as carbide, is now released by further amounts of hydrogen in the form $CH-$, CH_2- and CH_3- radicals, which then polymerize to a wide variety of hydrocarbons that may be adsorbed at first on the catalyst. As the length of the chain increases, the desorption of the compounds from the catalyst surface proceeds more and more slowly, thus increasing the interval of time available for complete hydrogenation by the hydrogen. These assumptions would easily explain the steady decrease in unsaturation of the products as the boiling point rises. Under certain conditions, high molecular weight hydrocarbons may be split into smaller fractions by a cracking process, thus establishing an equilibrium between polymerization and cracking."

A study of the formation of the CH_2-fragments was also made by S. R. Craxford. In this study, normal pressure synthesis was carried

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54/ Fischer, F., and Koch, H., Brennstoff Chem., vol. 13, 428, 1932.

55/ Craxford, S. R., Lecture Faraday Soc. April 1939, Brennstoff Chem., vol. 20, 263, 1939.

out both with carbon monoxide plus the customary hydrogen (ortho-para equilibrium) and with carbon monoxide plus para-hydrogen, to determine whether the ortho-para hydrogen equilibrium, for which the intermediate formation of atomic hydrogen is assumed, establishes itself during synthesis. It was found that there was ortho-para-hydrogen equilibrium when conversion of carbon monoxide did not occur, or resulted in the production of methane, and that there was no equilibrium when higher hydrocarbons formed. These observations led to the conclusion that atomic or chemisorbed hydrogen is not necessary for the formation of CH_2-chains and that the formation of chemisorbed hydrogen chains is considerably inhibited by the compounds present (carbides, adsorbed hydrocarbons). Molecular hydrogen acts on the individual carbon atoms of the carbides in question to give CH_2-radicals.

That the synthesis of CH_2-chains proceeds directly by polymerization of CH_2-radicals adsorbed on the catalyst surface, (and not by a gradual synthesis by the alternate action of carbon monoxide and hydrogen on the metal surface of the catalyst) is demonstrated by the fact that hydrocarbon formation can take place even in the absence of carbon monoxide, by action of acids on the carbides.

If the CH_2-radicals may definitely be considered as principal structural units of the hydrocarbons, then it necessarily follows that the hydrocarbons produced in the synthesis are mainly straight-chain compounds. The fact that only one out of 25 to 50 carbon atoms in the product is a tertiary carbon and that no quaternary carbon compounds were observed indicates that there are relatively few exceptions to the course assumed for the reaction.

It is known that in addition to paraffins the synthesis of aliphatic hydrocarbons also produces olefins. As shown in the case of cobalt, the amount of olefin formed is a function of the carbon monoxide-hydrogen ratio of the synthesis gas, and in the case of isosynthesis, especially of the temperature. In synthesis with catalysts of the iron group, αolefins appear as the primary synthesis products; double bond isomerization on the catalyst is possible, but proceeds more slowly than the synthesis. Consequently, under normal conditions αolefins predominate as reaction products. βolefins have higher octane numbers and are therefore more valuable as motor fuels. The so-called Ruhrchemie refining process is based essentially on an isomerization of primary olefins. Fuller's earth can generally be used as catalyst (300°).

2. Recent Observations on the Subject of Carbide Formation in the Synthesis of Hydrocarbons with Iron Catalysts

When hydrocarbon synthesis with iron catalysts (medium pressure) is to be carried out at low temperatures (200 to 250°) it is necessary that the iron catalysts be subjected to a preliminary treatment. The lower the synthesis temperature to be used, the greater the care that must be exercised in carrying out this pretreatment.

Two types of catalysts have proved particularly suitable for use in synthesis at low temperatures:

1. Precipitated catalysts.

56/ Koch and Richter, KWI for Coal Research, Mülheim, unpublished.

2. Fused catalysts (of the ammonia-catalyst type).

The large catalyst surface necessary for catalytic activity is determined in the first type by the method of precipitation. In the second type, the surface develops as a result of the reduction of the fused oxides.

To obtain precipitated catalysts of maximum activity, F. Fischer and H. Pichler (KWI) proposed pretreatment with carbon monoxide, or a carbon monoxide-hydrogen mixture, passed in a rapid stream over the catalyst at 1/10 atmosphere and 325°C. When mixtures of carbon monoxide and hydrogen were used, catalysts with a lower but satisfactory activity could be obtained by pretreatment at atmospheric pressure and temperatures between 225 and 250°C.

In connection with fused catalysts, the I. G. Farbenindustrie catalyst pretreatment requires reduction with hydrogen at a very high throughput (space velocity 3000) and a temperature of about 450° (48 hours).

The effect of pretreatment of iron catalysts with carbon monoxide or carbon monoxide-containing gases, such as water gas, must be compared with the effect of hydrogen. Preliminary treatment with gases containing carbon monoxide was described by Fischer and Pichler in their first patent application in the field of medium-pressure synthesis with iron catalysts. Subsequently, experiments were carried out by other workers for the purposes of obtaining active iron catalysts by other methods, such as pretreatment with hydrogen, or with hydrogen containing 1 percent of carbon monoxide, or even with inert gases (well dried ?) (TOM Reel 97, Bag 3451/24). It was later established by the Ruhrchemie that iron catalysts pretreated with water gas according to the KWI procedure showed less tendency towards methane formation than did catalysts reduced with hydrogen[57].

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[57] Work cited, footnote 34, p. 66.

Pichler and Merkel (Chemical and Magneto-Chemical Studies of Iron Catalysts - to be published) reported that iron catalysts pretreated with carbon monoxide contain a considerable amount of carbide having a Curie point at 260°; also that the activity of the catalyst and its carbide content are parallel within certain limits. X-ray examination of fused catalysts made at the I. G. showed that, after treatment with hydrogen as described above, (apart from promoters) these catalysts consist exclusively of α iron.

A contradiction appears to exist between these two observations since in the one case carbide seems essential for catalytic activity, whereas in the other it does not.

Since synthesis with different iron catalysts gives essentially the same products, provided other conditions are the same, and since in all probability the reaction mechanism is the same, it would be extremely interesting to clear up the apparent contradiction existing between the preceding statements. For this purpose the exact results of the research work leading to the different conclusions must be known. The following discussion is based on a portion of the experimental results obtained by Pichler and Merkel as well as on certain data of the I. G. Farbenindustrie:

When a precipitated iron catalyst containing 1 percent of copper and 1.5 percent of potassium carbonate was treated with carbon monoxide (1/10 atmosphere, 325°C.), it was converted first to Fe_3O_4 and then gradually to a new iron carbide (inflection point of the Curie curve, designated as C.P. in the following pages, 260°C.). After 12 hours, the iron of the catalyst may be considered for all practical purposes to be present entirely as carbide. Magnetite and free iron were absent, or present only in traces. On heating to 800°C., the 260° C.P. disappeared and was replaced by the 220° C.P. characteristic of the normal cementite produced by a decomposition reaction. The iron catalyst composed essentially of carbide (C.P. 260°) upon operation in the medium-pressure synthesis (235°, 11 atmospheres) possessed extremely high activity. Catalytic and magnetic behavior remained unchanged after 20 hours. After operating for some time, an increase in the Fe_3O_4 content, accompanied by a decrease in activity, was observed. Treatment of the fresh, completely carbided catalyst with molecular hydrogen at synthesis temperature (230° to 240°) gave no perceptible change in the composition of the catalyst in the course of one hour.

Carbide formation during pretreatment was also observed in a copper-free iron catalyst, but the process was considerably slower than when copper was present. Even after 25 hours, the carbide : magnetite ratio was only 6 : 10. In consequence, copper promotes not only reduction, but also carbide formation.

When this same Fe-1.5% K_2CO_3 catalyst was reduced first with hydrogen at 250° for 240 hours and then treated at low temperature (220°) with carbon monoxide [method of Bahr and Jessen, Ber. deut. chem. Gessel., vol. 66, 1238, 1939], it was found that after carburization with carbon monoxide for 219 hours, C.P. 260° carbide and magnetite were present in a 1 : 1 ratio. Using the same procedure with an Fe- 1% Cu- 1.5% K_2CO_3 catalyst, magnetic analysis showed that, in addition to the C.P. 260° carbide, another substance with a C.P. at 385° was present. When carburization at 205° was preceded by hydrogen reduction, the compound corresponding to the 385° C.P. was found to be by far the most abundant. A catalyst pretreated in this way showed no activity for synthesis. On heating to temperature higher than 300°, the C.P. 385° compound was converted to cementite (C.P. 220°).

Under the conditions of normal pressure synthesis with iron (Fe + 1/4% Cu, no special pretreatment, synthesis temperature 235°) the catalyst was first reduced to Fe_3O_4. This was followed by the very gradual formation of C.P. 260° carbide. After 120 hours (pretreatment period) the carbide to magnetite ratio reached 3 : 10. As the carbide content increased, contraction also increased (synthesis gas $CO:H_2$ = 1:2) from zero to 34 percent. (Towards the end of the pretreatment period, almost complete carbon monoxide conversion was obtained.)

The experiments showed that, in addition to the Fe_3C carbide (cementite, 220° C.P.) which alone is stable at temperatures above 300 to 400°, there exist two thermally unstable carbides, with C.P. 260° and 385°, respectively, first of which was obtained with particularly high yield by carbon monoxide treatment of the unreduced iron catalyst, and the second by carburization at low temperatures of a catalyst previously reduced with hydrogen.

Should the two carbon-rich carbides differ in chemical composition, then the data published in the literature with reference to the iron to carbon ratio of the carbon-rich carbide must be incorrect. The explanation is that under the conditions used by Bahr, Jessen, and others to prepare their Fe_2C, the C.P. 260° carbide always forms (as shown by magnetic studies by Pichler and Merkel) in addition to the C.P. 385° carbide. The composition was always determined from the total content of iron and carbon present as an iron-carbon-rich compound. The reproducibility of the results obtained indicates that these carbides both represent modifications of Fe_2C. Experiments on this point are still in progress.

Two reports of the I.G. Farbenindustrie[58] recently discovered among the documents of the War Department, read as follows:

"As long as 12 years ago, Fischer added copper to his iron catalyst in order to facilitate reduction. X-ray studies initiated by Dr. Halle, and continued and completed by Dr. Herbst, showed that in addition to promoting reduction, copper plays another important part in the synthesis. In the course of the synthesis, with our standard catalyst,

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[58] Group leader conference Ludwigshafen, TOM Reel 26, Bag 2463 and Report Dr. Wenzel, TOM Reel 134, II/10).

a new hexagonal carbide, Fe_2C, not mentioned in the literature, is formed which must be considered as essential for satisfactory activity of the catalyst. Over a period of time, and especially at high temperature this new hexagonal catalyst was found by Dr. Herbst to be converted into the familiar Fe_2C carbide of Hägg. The addition of copper has a marked inhibitory effect on this change and copper may therefore be considered to act as stabilizer for an intermediate state of the catalyst first arising during synthesis. The addition of 2 percent of copper, for instance, raises the conversion temperature by about 50°.

"Experiments at Oppau (Anm. Lab. Ber. 1676 Dr. Herbst) show that hexagonal iron carbide Fe_2C forms in KW 17 (NH_3 fused catalyst) during synthesis and that at temperatures above 290° it is converted into the inactive Hägg Fe_2C.

Both these reports from the protocol of the I.G. Farbenindustrie show that carbide was also present in the I.G. catalyst. Following the usual energetic hydrogen reduction of the I.G. catalyst to α iron, carbide formation is reported in the first stage of the synthesis (it is not indicated precisely whether carbide formation occurs before final synthesis pressure is reached). The reports also show that X-ray investigation at the I.G. has established the presence of two different carbon-rich carbides, one of which is designated as "inactive".

This "inactive" carbide is considered to be identical with that described by Hägg,[52/] who prepared his carbide according to the

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[52/] Hägg, Zeitschrift f. Kristallographie, vol. 89, 92, 1934.

procedure of Bahr and Jessen, by carburization of an iron oxide which was first reduced with hydrogen for 1080 hours at 250°C. For a carburization temperature of 225°, x-ray examination gave very intense lines. An iron catalyst carburized in the same way by Pichler and Merkel was found on magnetic investigation to consist mainly of C.P. 385° and C.P. 260° carbides. In addition to the lines of the carbon-rich carbide, Hägg reported faint lines for Fe_3C and Fe_3O_4. At higher temperatures, the amount of Fe_3C increased at the expense of the new carbide. It is interesting to note that the results obtained from x-ray analysis of the Hägg carbide are not identical with the lines reported by Hofmann and Groll[60] for the carbide they obtained by a very similar process. The differences are not well defined. In the light of the new studies at the KWI and the I.G., it is probable that in both cases the two different carbon-rich carbides are present.

According to work at the I.G., an iron catalyst which had undergone extensive hydrogen reduction when operated for the synthesis gave hexagonal Fe_2C, which was eventually transformed into the Hägg carbide at higher temperatures. Small amounts of copper are reported to have a stabilizing effect on the hexagonal carbide. The fact that the different carbides apparently prepared under the same conditions by different carbides apparently prepared under the same conditions by different research workers, did not prove to be identical, indicates that, in addition to copper, there may be other factors capable of influencing the formation and decomposition of the carbide. Although the limits

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[60] Hofmann and Groll, Zeitschrift Anorg. Chemie, vol. 191, 414, 1930.

of existence for the two new carbides and particularly the differences in their behavior during synthesis have not been clearly determined as yet, formation of one or the other carbide is dependent upon the following factors: composition of the carburizing gas, temperature, pressure, and presence of promoters. Thus, it might be important to know whether the iron preparation was completely reduced before carburization, or whether a certain amount of oxide was still present. The alkali content of the iron catalyst may also be an influential factor.

In any case, the presence in the active iron catalyst of a carbide having a higher carbon content than cementite may now be considered as definitely established. However, this should by no means be considered proof that this carbide constitutes an intermediate product in the hydrocarbon synthesis. For instance, the fact established by Pichler and Merkel that the formation of their carbides is relatively slow, that molecular hydrogen acting at a synthesis temperature of 240° for a period of an hour produces no appreciable change in the composition of the carbide catalyst, and that under these conditions no formation of higher hydrocarbons results from the action of hydrogen on the carbide, all constitute evidence against this hypothesis.

Discussion of all the arguments for or against the so-called "carbide theory" would exceed the scope of the present paper. Apart from kinetic considerations, the fact that ruthenium catalysts produce hydrocarbon compounds without forming carbides, and the fact that these are the same type of hydrocarbons as are produced by iron and cobalt catalysts form strong evidence against the necessity of intermediate carbide formation.

In isosynthesis, in the presence of oxide catalysts, the hydrocarbons form at the active catalyst surface by way of oxygenated compounds, especially alcohols. The formation of alcohols in medium-pressure synthesis with iron catalysts and the increase in their yields at low temperatures and short reaction times, indicates a similar reaction process.

It is possible that the primary synthesis products are surface compounds which in the case of certain metallic catalysts, by their structure and optimum conditions of formation closely resemble true carbonyls or hydro-carbonyl compounds (ruthenium), whereas with oxide catalysts for instance, oxygenated compounds may be assumed to form, very probably by way of formaldehyde, as the result of a purely surface reaction.

Since the different studies of iron catalysts have established a relation between their activity and the amount of carbon-rich carbide present, it may be assumed that this carbide is an important factor in the specific structure which is necessary in an active iron catalyst for the hydrogenation of carbon.

3. Pretreatment and Carbide Formation in Cobalt Catalysts

It will be seen from the preceding section that active iron catalysts for the hydrocarbon synthesis may be prepared by preliminary treatment with carbon monoxide, with hydrogen, and with a mixture of carbon monoxide and hydrogen, under conditions different from those prevailing during synthesis. On the other hand, hydrogen reduction is the only procedure for the preparation of an active copper-free cobalt catalyst for hydrocarbon synthesis. For the cobalt-kieselguhr catalyst in general use, the optimum reduction temperature depends on the kieselguhr content. The temperature must be kept as low as possible to avoid sintering (low conversion for each throughput of hydrogen limits the amount of heat liberated by the exothermal reaction, thus avoiding a dangerous increase in temperature). For a cobalt to kieselguhr ratio of 1:1, the reduction temperature is 365°; for a 1:2 ratio, it is 395°. The hydrogen should be as free as possible of oxygenated compounds such as water, carbon dioxide, and carbon monoxide and the space velocity should be high. Industrially, the upper limit for the carbon monoxide content is set at 0.05 percent. When recycle hydrogen is used, carbon dioxide and water, formed by decomposition of the carbonate and by reduction of the oxide, respectively, are removed as completely as possible by cooling and passing through silica gel. All these precautions are designed to obtain the desired degree of reduction at the lowest possible temperature in the shortest possible time. Complete reduction of the cobalt catalyst is not desirable. Too highly reduced cobalt catalysts show excessive initial activity (methane formation) and a shorter life than cobalt catalysts which still contain some oxide. Industrially-prepared cobalt catalysts are reduced 50 to 65 percent.

The reason why the hydrogen used in reducing the cobalt catalyst must be as free as possible of carbon monoxide has not been fully explained. The assumption made by various workers that the methane formed in the presence of carbon monoxide leads to overheating and consequently to sintering of the catalyst is not entirely satisfying. It seems more likely that the water and carbon dioxide which accompany the formation of methane have an unfavorable effect on the reduction process.

In the course of synthesis, Co_2C carbide forms in the catalyst. Generally speaking, its fraction is smaller than the fraction of iron carbide in precipitated iron catalysts.

The carbide and metal content of cobalt catalysts was the subject of a detailed study by Meyer and Schirmacher[61].

The question of whether cobalt carbide is to be considered as an intermediate product in hydrocarbon synthesis leads to considerations similar to those discussed in connection with iron carbide.

Recent kinetic studies of cobalt catalysts[62] do not support the theory of intermediate carbide formation. These works establish the fact that steady-state carbide formation proceeds at a much slower rate than the synthesis.

Thus, as regards cobalt catalysts also, the question of the part played by the carbide in the hydrocarbon synthesis cannot be considered as solved.

61/ Meyer and Schirmacher, the Mülheim Institute (unpublished, 1934).

62/ Crawford and Rideal, Jour. Chem. Soc., 1939, 1604.
Eidus and Zelinsky, Bull. Acd. Sci. URSS, 1942, 45.
Weller, S., Kinetics of Carbiding and Hydrocarbon Synthesis with Cobalt Fischer-Tropsch Catalysts, Jour. Am. Chem. Soc. (in press).

4. Possible Intermediate Formation of Carbonyls in the Synthesis of Hydrocarbons

The extent to which well defined carbonyls, or surface compounds with carbon monoxide, act as intermediates in synthesis with nickel, cobalt, and iron cannot be definitely stated. However, the possible occurrence of intermediate compounds of the carbonyl type should not be arbitrarily discarded[63].

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[63] O. C. Elvins, Jour. Soc. Chem. Ind., vol. 46, 473 T, 1927.

In the case of nickel, the carbonyl forms even at a carbon monoxide pressure of less than 1 atmosphere.

The condition of the equilibrium

$$Fe + 5\,CO \rightleftharpoons Fe(CO)_5$$

has been the subject of a publication by H. Pichler and H. Walenda[64].

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[64] Pichler, H., and Walenda, H., Brennstoff Chem., vol. 21, 133, 1940.

The authors showed that at a temperature of 170°, iron carbonyl starts to form at a carbon monoxide pressure as low as 10 atmospheres. At 210°, the corresponding pressure is 30 atmospheres; at 260°, 100 atmospheres. As the temperature rises, the amount of stable iron carbonyl in equilibrium decreases, but the reaction rate increases. Maximum carbonyl formation was observed at about 200°.

Ruthenium, as shown particularly by the work of Mond and Manchot[65] forms carbonyls at higher pressures than iron, cobalt and nickel.

In this connection, Manchot[66] draws attention to the similarity between ruthenium and iron, and between their carbonyls which is attributed to their electron configuration. Ruthenium also forms a volatile pentacarbonyl, $Ru(CO)_5$ that is very easily transformed into the more stable ennea-carbonyl ($Ru_2(CO)_9$ which, however, decomposes at 200°.

Inspection of table 28 leads to the definition of the relations between carbonyl formation and synthesis; optimum synthesis conditions prevail at pressures just below those at which (at the corresponding temperatures) the tendency towards the formation of volatile carbonyls becomes so great that deterioration of the catalyst results. In other words, conditions must be chosen in such a way that the rate of formation of volatile carbonyls remains somewhat less than that for the reaction of the supposed intermediate carbon monoxide compounds with hydrogen.

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[65] Mond, R. L., Hirts, and Cowap, Zeitschr. Anorg. Chem., vol. 68, 218, 1910.
Mond, R. L., and Wallis, A., Jour. Chem. Soc., vol. 121, 30, 1921.
Mond, R. L., Chim. et. Ind., vol. 21, 690, 1929.
Manchot, Zeitschr. Anorg. Chem., vol. 226, 385, 1936.

[66] Manchot, W., and Manchot, W. J., Z. Anorg. Chem., vol. 226, 391, 1936.
Manchot, W., Liebigs Annalen, vol. 470, 266, 1929.

Table 28. - Optimum Pressures of Synthesis Gas with Different Catalysts. Pressures for which Undesirable Formation of Carbonyls, or Hydrocarbonyl Compounds occur at the Synthesis Temperature

Syn. gas pressure (atm.)	Ni	Co	Fe	Ru
Optimum for synthesis	1	5-30	10-30	100-1000
Undesirable carbonyl formation	>1	>30	>30	Under the conditions of the synthesis, carbonyls form on the surface of the catalyst

Especially in the case of ruthenium, which has proved to be an exceptionally good catalyst for the synthesis of higher hydrocarbons, the agreement between the optimum temperature and pressure conditions for the synthesis and those for carbonyl formation (partial CO pressure) is striking.

No ruthenium carbide is known to form under the conditions of the synthesis. At the high pressures used in ruthenium synthesis, the hydrocarbons formed are of a higher molecular order than those obtained in normal and medium pressure syntheses with cobalt and iron. However, the fact that in other respects the formation of hydrocarbons in the presence of ruthenium is essentially the same as in the syntheses with catalysts of the iron group has again raised the question of carbides versus carbonyl-like surface compounds as intermediates in the synthesis of hydrocarbons from carbon monoxide and hydrogen.

5. High-Pressure Synthesis of Alcohols

The synthesis of alcohols at high pressures and relatively high temperatures requires catalysts whose hydrogenating action is weaker than that of the catalysts used for the synthesis of hydrocarbons. Certain oxides are suitable hydrogenating agents, such as zinc oxide, or zinc oxide-chromium oxide, in the case of methanol.

67/ I.G. Farbenindustrie DRP 415686, 273787.

When alkali is present in the zinc oxide, higher alcohols form in addition to methanol.

68/ Natta and collaborators, G. Chim. ind. appl., vol. 12, 13, 169, 1930; vol. 13, 317, 1931; vol. 14, 217, 1932.
Frolich, K., and Cryder, S., Ind. Eng. Chem., vol. 22, 1051, 1930.

As in the aliphatic hydrocarbon series, in the synthesis of alcohols only the first member of the homologous series can be prepared by itself, whereas the higher homologues always occur in mixtures; the unique position of methanol and methane results from the absence of a carbon to carbon bond.

The reaction

$$CO + 2H_2 \rightleftharpoons CH_3CH$$

obeys the rules for an equilibrium and can be controlled easily. At atmospheric pressure and temperatures above 300°, the equilibrium shifts completely to the carbon monoxide-hydrogen side, whereas at 100 atmospheres and 300° it lies almost entirely on the methanol side.

As regards the course of the reaction, it appears extremely probable that carbon monoxide and hydrogen first react on the active catalyst surface to form formaldehyde which is then hydrogenated to methanol in a second step. The intermediate appearance of formaldehyde can be observed when methanol decomposes.

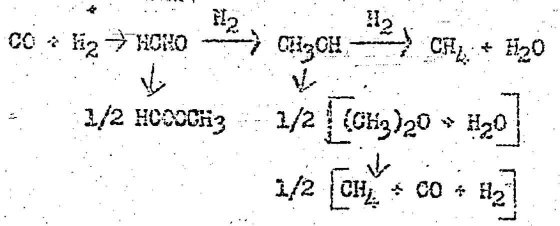
69/ Frolich and collaborators, Ind. Eng. Chem., vol. 20, 694, 1327, 1928; vol. 21, 109, 867, ~~[illegible]~~, 1929. Vol 22, 1051, 1930
Audibert and Haineau, Ind. Eng. Chem., vol. 20, 1105, 1928.
Dohse, Z. physik. Chem. Abt. B., vol. 8, 159, 1930.
Pichler, H., Brennstoff Chem., vol. 24, ~~27~~, 1943.
Brown and Galloway, Ind. Eng. Chem., vol. 21, 310, 1929; vol. 22, 175, 1930.

In addition to water, the byproducts of methanol synthesis contain methyl formate, dimethyl ether, and small amounts of methane and carbon dioxide. Methyl formate is synthesized by way of formaldehyde, dimethyl ether by the loss of water from methanol. The equilibrium

$$2\ CH_3CH \rightleftharpoons CH_3CCH_3 + H_2O$$

has been studied repeatedly and the free energy of the reaction determined.

The overall reaction may be represented as follows:



$$\begin{tikzcd} CO + H_2 \arrow[r] & HCHO \arrow[r, "H_2"] \arrow[d] & CH_3CH \arrow[r, "H_2"] \arrow[d] & CH_4 + H_2O \\ & 1/2\ HCOOCH_3 & 1/2\left[(CH_3)_2O + H_2O\right] \arrow[d] & \\ & & 1/2\left[CH_4 + CO + H_2\right] & \end{tikzcd}$$

The mechanism for the formation of the higher alcohols has been studied by Franz Fischer, Mittasch, Frölich and Cryder, Parks and Huffmann, among others.

In general, these various theories are based on the assumption that methanol forms by way of formaldehyde. In 1924, Franz Fischer made the assumption, in connection with synthol synthesis, that methanol takes up carbon monoxide to give acetic acid, which is then reduced by hydrogen to acetaldehyde or ethyl alcohol. Ethyl alcohol would produce propyl alcohol by a similar procedure, and so on. This explanation of the reaction mechanism was in accord with the fact, shown in table 3, that the intermediate products enumerated do actually occur simultaneously in the synthesis of synthol.

According to Frolich and Cryder, alcohols form as a result of single stage dehydration:

$$2\ CH_3OH = C_2H_5OH + H_2O$$

$$C_2H_5OH + CH_3OH = C_3H_7OH + H_2O, \text{ etc.}$$

Parks and Hufmann studied the free energies of the different ractions, or intermediate reactions. However, the most probable reaction path has yet to be definitely established.

6. The Reaction Mechanism of the Isosynthesis

Thorium oxide is the best catalyst for isosynthesis. Addition of aluminum oxide and, in certain cases, small amounts of alkali, increases its activity. Branched-chain hydrocarbons were also obtained with a series of oxide catalysts such as zirconium oxide, cerium oxide, as well as with certain mixed catalysts such as zinc and aluminum oxides whose individual components are not suitable for isosynthesis. In contrast to syntheses with catalysts of the iron and platinum groups, where oxides of this type are used as promoters, in isosynthesis the oxides are the actual catalysts for the reaction. There can be no question here of intermediate formation of carbides or specific carbonyls. The primary formation of oxygenated organic compounds as a result of surface reactions appears well established. Methanol, isobutyl alcohol, and dimethyl ether are in evidence. The dehydrating action of the catalyst transforms them into olefins, which in turn are polymerized and hydrogenated, under the conditions of operation, to give a variety of hydrocarbons.

The composition of the products formed by isosynthesis does not depend on any isomerization equilibria. As will be seen from figure 23, isobutane represents a much higher percent of the C_4 fraction than would correspond to the C_4H_{10} equilibrium. (For purposes of comparison, the iso-C_4 content for synthesis with iron and with cobalt is also given in figure 23.) In the same way, the C_5 fraction has a higher isopentane content, and the C_6 fraction a higher content, particularly of 2,3-dimethyl butane than would be expected for isomerization equilibria. Consequently, in the synthesis of hydrocarbons from oxygenated compounds, these products, or the corresponding olefins, represent primary hydrocarbons which may undergo further transformation as a result of isomerization, polymerization, alkylation, and aromatization.

7. Hydrogenation of Carbon Dioxide[70]

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[70] Pichler, H., Brennstoff Chem., vol. 24, 39, 1943.

Methanol and methane differ from their homologues not only in that they can be synthesized from carbon monoxide and hydrogen without

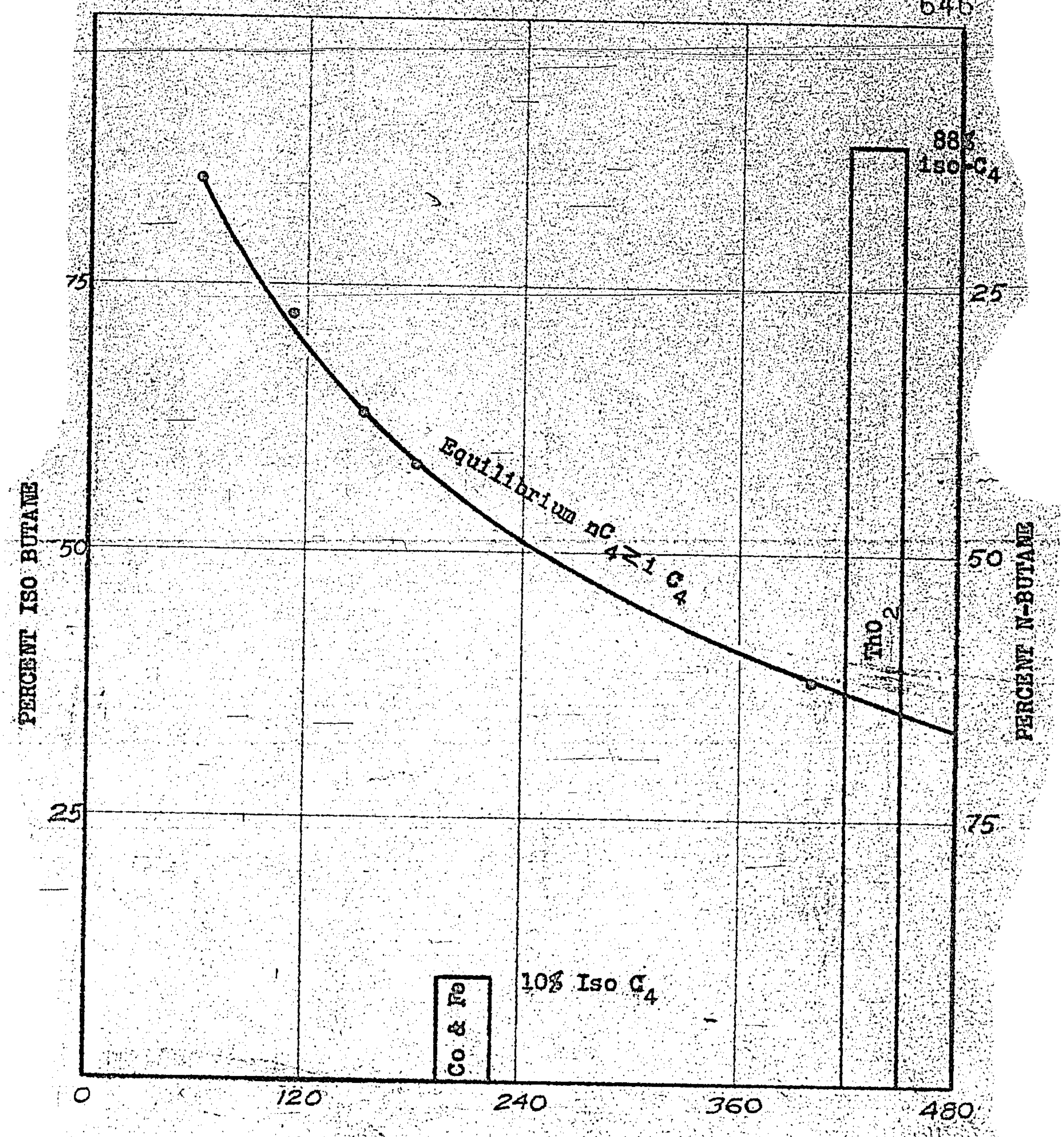
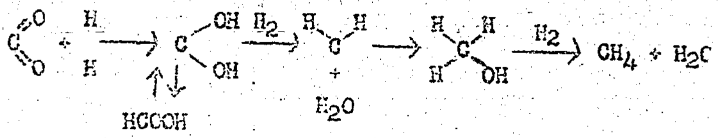


Figure 23: The equilibrium between n and Iso Butane and the Iso C_4 content of various syntheses.

the simultaneous formation of higher homologues, but they can also be synthesized from carbon dioxide and hydrogen without going through the intermediate formation of carbon monoxide. Whereas, in the case of their homologues, the existence of carbon monoxide surface compounds is assumed, it seems probable that the formation of methane and methanol is associated with the occurrence of activated hydrogen at the catalyst surface. Hydrogenation of carbon dioxide then results in the formation of methanol or methane, very probably by way of formic acid and formaldehyde. The peculiar behavior of formic acid, whose production from carbon dioxide and hydrogen has been established by a number of workers, would indicate the existence of the unstable isomer, dihydroxymethylene. The reactions accompanying the direct hydrogenation of carbon dioxide may be represented as follows:



The first step consists in the formation of activated hydrogen at the catalyst surface. As already indicated, this process is delayed by the presence of carbon monoxide. With certain catalysts, such as ruthenium, mixtures of carbon dioxide and hydrogen react at temperatures as low as 100° to give methane. Experiments with mixtures of carbon dioxide, carbon monoxide, and hydrogen gave no such reaction up to 150°. At this temperature, carbon monoxide began to react, whereas no reaction of carbon dioxide could be observed until temperatures at which carbon monoxide had disappeared almost completely by reaction with hydrogen.

It is because of this property of carbon dioxide that carbon monoxide-hydrogen mixtures containing carbon dioxide can be used for the synthesis of higher hydrocarbons, without losing a portion of the hydrogen through reaction with carbon dioxide to methane; in other words, carbon dioxide acts like an "inert gas" when passed over the catalyst.

The intermediate formation of unstable dihydroxy-methylene has also been postulated in connection with biologic reactions. The formation of formaldehyde as intermediate in the assimilation of carbon dioxide in nature appears definitely established. Willstätter and Stoll reported that: "There is nothing theoretical in the fact that formaldehyde represents the reduced state of carbonic acid reached in the course of assimilation; theoretical considerations apply only to the manner in which the deoxidation of the carbonic acid proceeds."

The fact that formaldehyde may be considered as the basic material of the carbohydrates suggests a certain analogy between the processes accompanying the assimilation of carbon dioxide in nature and the mechanism governing the catalytic hydrogenation of the oxides of carbon.

8. Summary

The temperature-pressure diagram of figure 24 shows the optimum regions of operation for the various processes used in the hydrogenation of carbon monoxide. The facts presented in the preceding sections suggested that the various procedures be considered from a common point of view.

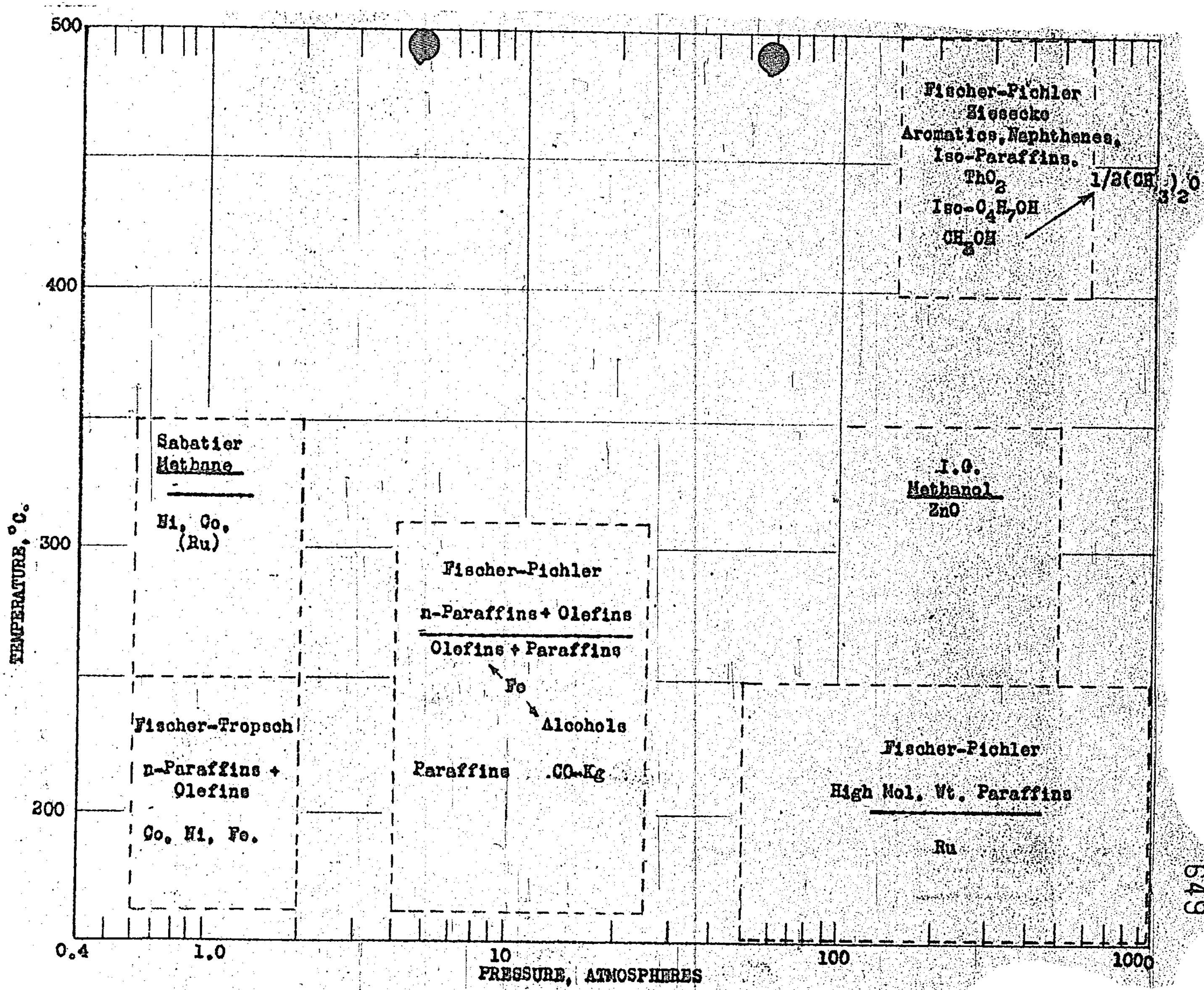


Figure 24: Pressure-temperature areas for different synthesis processes.

Each of the catalysts in figure 24 has a specific action towards hydrogen and carbon monoxide as shown by the tendency to form methane or higher hydrocarbons, or the tendency to form alcohols, not to mention the ability to hydrogenate, to dehydrate alcohols, to polymerize olefins, and to promote reactions such as isomerization, alkylation, cyclisation, etc. Moreover, by suitable choice of synthesis conditions these characteristic properties of the catalyst may be oriented in one particular direction. For instance, the less the hydrogenating power of a given catalyst is, the higher the temperature or the pressure, or both, at which it must be operated in order to obtain a given reaction. Addition of promoters also serves to orient the properties of the catalyst in one way or another.

Under the conditions of the Fischer-Tropsch synthesis, that is, at 200° and atmospheric pressure, cobalt, and to a lesser extent iron, were suitable catalysts for the synthesis of higher hydrocarbons. Nickel, which has a much greater hydrogenating action than cobalt or iron and tends in consequence to form methane, could not be used for the synthesis of higher hydrocarbons until the use of kieselguhr as a means of diluting the metal concentration in the catalyst had been established. As the temperature rises, the hydrogenating power of the catalysts increases, and is accompanied by a decrease in the tendency to fix carbon monoxide. Eventually a region is reached where methane is the sole product (Sabatiers and Senderens); the intermediate formation of "activated" hydrogen, for which nickel is the best catalyst, is assumed.

If the pressure is increased under the initial conditions of the Fischer-Tropsch synthesis, a region is reached first for nickel, later for cobalt and iron, and finally, at much higher pressures for ruthenium, in which the carbonyl is formed. The use of nickel at even slightly elevated pressures is precluded owing to the loss of nickel through the formation of volatile carbonyls. Cobalt can be operated at somewhat higher pressures (up to 20 or 30 atmospheres) but owing to its high degree of activity it must be diluted with increasing amounts of inert material, for instance, with kieselguhr as the pressure increases. No such "dilution" is necessary with iron, whose activity is lower. Satisfactory conversion with respect to rate of reaction was obtained with this catalyst at 10 to 20 atmospheres. The formation of ruthenium carbonyl occurs only at very high pressures of carbon monoxide and as a result this catalyst can, and probably should, be operated at high pressures. Since the tendency to form high molecular-weight compounds increases with the pressure, the principal products obtained with ruthenium catalysts are high molecular-weight paraffins. The synthesis pressures used with this catalyst lie within a region in which there is a tendency towards the formation of volatile carbonyls. However, the catalyst may be operated over long periods without deterioration because the action of carbon monoxide on ruthenium results in the formation of a carbonyl which is fixed at the surface of the catalyst and inhibits any further action of carbon monoxide to form carbonyl. In addition, it is very probable that the hydrogen which is also present always reacts at a sufficient rate with the surface carbon monoxide producing, methylene (CH_2) radicals.

Oxide catalysts in general show a smaller degree of activity towards carbon monoxide and hydrogen than the metal catalysts. Higher pressures and temperatures are required for conversion, which is the result of surface reactions. Whereas the high hydrogenating power of cobalt, nickel, and ruthenium orient the hydrogenation of carbon monoxide almost entirely towards hydrocarbons, and the less active iron favors the formation of larger amounts of alcohols only at especially low temperatures and short contact times, oxide catalysts favor the formation of alcohols.

Just as conditions can be adjusted so that nickel produces methane as sole hydrocarbon, so, in the case of zinc oxide, methanol may be produced as the only alcohol. Similarly, just as methane is the sole hydrocarbon that can be formed by direct synthesis from carbon dioxide and hydrogen, so methanol is the only alcohol of which this is true.

The fact that methane and higher hydrocarbons may be produced by differing reactions paths is particularly evident when working with ruthenium catalysts, where the optimum region for the formation of higher hydrocarbons is widely separated from that of methane.

Addition of alkali to the catalysts of the iron group shifts the reaction towards the formation of higher boiling compounds. In a similar manner, addition of alkali to zinc oxide favors the formation of higher alcohols. When added to thorium oxide, it also results in the formation of higher boiling hydrocarbons.

The fact that hydrocarbons constitute the chief product of isosynthesis results from the intense dehydrating action of thorium oxide and related catalysts. In the region of operation for this synthesis, low temperatures produce high yields of alcohols. A rise in temperature at first increases the olefin yield; then, as the hydrogenating power of the catalyst increases, iso-paraffins are formed. A further rise in temperature produces naphthenes and finally, because of their high thermal stability, aromatics.

9. Conclusion

It has been shown that widely differing catalysts can cause a reaction between carbon monoxide and hydrogen. The nature of the products formed varies considerably, according to the reaction conditions chosen. Results of a series of recent experiments have led to the abandonment of the theory that carbide catalysts produce hydrocarbons and oxide catalysts, alcohols. Similarities in reaction of essentially different catalysts, and differences observed for the same catalyst under various conditions caused this change in theory.

In a very general way, it may be said that as a first step in the synthetic process, carbon monoxide and hydrogen are chemisorbed on the catalyst surface. The chemisorption of hydrogen leading to the formation of methane is impeded by that of carbon monoxide. According to the type of catalyst and the synthesis conditions, carbon monoxide can participate in the formation of a wide variety of compounds on the catalyst surface, ranging from loosely bound surface compounds to well defined carbonyls.

The breaking of the carbon to oxygen bond constitutes a second step in the synthesis, producing in certain cases the elimination of oxygen (as water) and the formation of carbides, or even of free carbon.

The third stage involves the action of hydrogen. According to the conditions of the synthesis which determine the rates of the first, second, and third steps, the effect of hydrogen becomes apparent at different intervals, giving ~~use~~ rise to a series of reactions which proceed simultaneously, although at different rates, and result in the conversion of the weak metal to carbon monoxide bonds, of the carbonyl, of the weakened carbon to oxygen bonds and of the carbide.

Office of Synthetic Liquid Fuels
Research and Development Division
U. S. Department of Interior
Bureau of Mines
Central Experiment Station
Pittsburgh, Pa.
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