



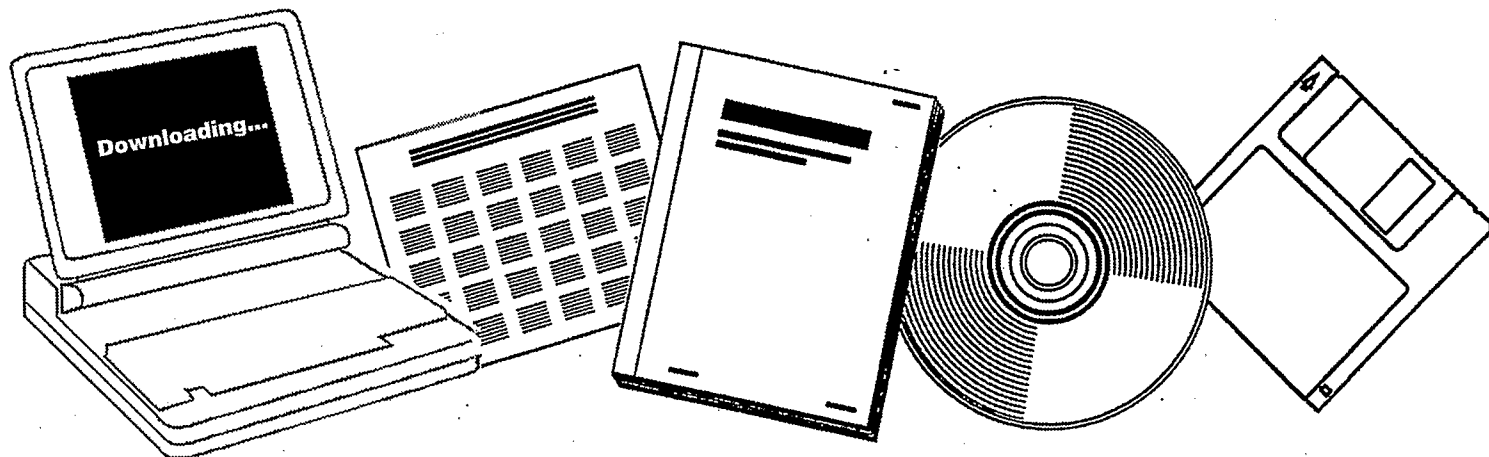
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HIGH PRESSURE HYDROGENATION OF CARBON MONOXIDE TO PREFERENTIALLY ISOPARAFFINIC HYDROCARBONS (ISOSYNTHESIS). PART I

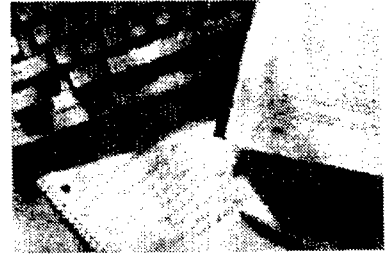
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High Pressure Hydrogenation of Carbon Monoxide to Preferentially Isoparaffinic Hydrocarbons ("Isosynthesis") Part I*

Affiliation: Kaiser-Wilhelm Institute for Coal Research, Mülheim an der Ruhr

ORIGINAL TITLE

Über die Hochdruck-Hydrierung von Kohlenoxyd zu vorzugsweise isoparaffinischen Kohlenwasserstoffen ("Isosynthese") I. Teil.*

AUTHORS

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HIGH PRESSURE HYDROGENATION OF CARBON MONOXIDE TO
PREFERENTIALLY ISOPARAFFINIC HYDROCARBONS ("ISOSYNTHESIS")

PART I

Introduction

A variety of demands are made of a high grade gasoline, especially an aviation fuel, including primarily a certain boiling range, purity, storage stability and low temperature stability. In order to achieve the highest possible performance, it is also important to have good compressibility, i.e., a high octane rating, a good supercharging curve and a high lead sensitivity of the fuel [1].

- The highest requirements are met by isoparaffinic hydrocarbons which have a higher compression strength as their molecular structure becomes more compressed, preferably in the presence of tertiary carbons or, even better, quaternary carbons. High octane ratings are also obtained with aromatics and, as with isoparaffins, this is largely independent of the boiling point of the individual hydrocarbons.

Of the two antiknock type of hydrocarbons, the isoparaffins and aromatics, the latter are obtained as byproducts of the coking process and also in high-pressure hydrogenation of coal. So far, Germany has lacked the necessary raw material basis for production of sufficient amounts of branched isoparaffins that are of primary value for the combustion engine [2].

Important starting materials for the production of high grade aviation gasoline include isobutene and isobutane. The former can be produced by polymerization [3] followed by

hydrogenation, while the latter is produced by alkylation, e.g., with n-butene [4] to yield the isooctane which is in especially high demand as an aviation fuel. With the methods presently known for producing liquid fuels on the basis of carbons, iso-C₄ hydrocarbons are obtained only as subordinate byproducts. In high-pressure hydrogenation of coal according to the Bergius-I. G. Farbenindustrie A.G. method [6] they constitute varying amounts of the total reaction products, depending on the reaction conditions, but in normal pressure synthesis* according to Fischer-Tropsch method [6] and in medium pressure synthesis according to the Fischer-Pichler method [7] (scaled up to an industrial level by Ruhrchemie A.G. [8]), they amount to about 0.5 to 1%.

Of the methods of producing isohydrocarbons, apart from a few organic preparative methods and polymerization of olefins, the main ones that should be mentioned are catalytic isomerization or cracking normal paraffins in the presence of aluminum halides [11]. In addition, isobutene which is important for production of valuable engine fuels can be obtained from isobutyl alcohol which can in turn be synthesized from carbon monoxide and hydrogen on alkalized zinc catalysts. The main product of this process is methanol, but isobutyl alcohol constitutes about 20-30 wt% of the liquid reaction products [12].

*A comprehensive investigation of the hydrocarbons [illegible] obtained below 100°C in normal pressure synthesis on cobalt catalysts was conducted by H. Koch and F. Hilberath [9]. Of the saturated hydrocarbons, 7.5% isobutane was found in the C₄ fraction by fine distillation, the C₅-C₇ fraction yielded the main paraffins n-pentane, n-hexane and n-heptane, and various hydrocarbons with single branches such as methylbutane, 2-methylpentane, 3-methylpentane, 2-methylhexane and 3-methylhexane. Paraffins with multiple branches, if obtained at all, were found only in traces. Recent studies from the local institute concerning the composition of the synthesis products will soon be reported in detail in this journal. Excerpts of these findings have already been published by H. Koch [10].

In the past there has not been a process based on coal or its gasification products whereby suitable isoparaffins are obtained directly as main products. The following studies have grown out of the work by F. Fischer in 1940 as part of his research into the synthesis of aromatic hydrocarbons. The outcome is a new synthesis which was given the name "isosynthesis". The starting materials are carbon monoxide and hydrogen, as in the synthesis of normal paraffins. In contrast with the known hydrocarbon synthesis process using cobalt and iron catalysts, however, different catalysts are required here, namely certain oxides, primarily thorium oxide and considerably higher reaction temperatures and pressures are necessary. Accordingly, the reaction process is fundamentally different. This synthesis was described for the first time by Franz Fischer [6] in a lecture in 1943 titled "Survey of the syntheses from carbon monoxide and hydrogen".

Experimental part

1. Experimental setup

The setup for carrying out the experiments consisted of the system diagrammed in Figure 1:

1. A 1000 atm compressor from the company Andreas Hofer
2. A high-pressure storage tank for pressures up to 1000 atm. A high-pressure tube from the company Krupp with an inside diameter of 275 mm and a length of 3.5 m was used for this purpose. It was sealed at both ends with screw-in plugs. At the institute workshop, a brass lining was provided to prevent the formation of carbonyls and this brass lining also served the purpose of providing a seal with respect to the plugs.

3. A battery of 6 steel cylinders which were used together with the 1000 atm storage tank at pressures below 350 atm in order to increase the pressure constancy.

4. The reaction apparatus, which was a pressurized tube lined with copper and resting in a metal block, generally an aluminum block.

5. The pressurized receiving vessel for condensation of most of the liquid reaction product which was kept at a temperature slightly higher than 31°C (critical temperature) to prevent liquefaction of the carbon dioxide.

6. A vessel containing activated carbon to remove the remainder of the liquid reaction product and gas oil from the end gas at normal pressure.

The small-scale experiments in the laboratory were generally carried out at a gas throughput of 10-20 L/hr (based on atmospheric pressure). Larger scale experiments were carried out with gas throughputs of up to about 3000 L/hr. The amount of incoming gas was determined by measuring the expanded end gases and the contraction values resulting from the change in the nitrogen content of the starting gas and the end gas.

Of the reaction products which were removed from the end gas by cooling and with activated carbon, the composition of the gaseous hydrocarbons was always determined by low-temperature distillation and the composition of the liquid hydrocarbons was determined by the fine distillation, usually of the hydrogenated products (see analytical section). Of characteristic tests, the index of refraction, density, etc., were determined on the individual fractions of liquid hydrocarbons. In addition,

after appropriate distillation and adjustment of the vapor pressure, the gasolines thus produced were tested in an I.G. test engine according to the motor method to determine their knock rating in a crude state and also in a hydrogenated state, with and without the addition of lead tetraethyl.

II. General information about the catalysts in isosynthesis

If water gas is passed through an empty unalloyed steel tube (inside diameter 12 mm, heated length 300 mm, throughput 20 E/hr) at a pressure of 30 atm and a temperature of 450°C, for example, carbon monoxide and hydrogen will be converted, yielding mainly carbon, carbon dioxide and lower hydrocarbons, especially methane.

Table I shows the composition of the starting gas and end gas of such an experiment which was operated for 30 days. These results show that small amounts of heavy hydrocarbons and homologs of methane were formed (as seen from the carbon number of the saturated hydrocarbons). In a determination of yield, 8.5 g C₃ hydrocarbons, 7.4 g C₄ hydrocarbons and 2 g gasoline were obtained per standard cubic meter of water gas. There is a gradual drop in gas conversion during prolonged operation time in accordance with the buildup of carbon in the tube.

A low-temperature distillation of the C₃-C₄ fraction yielded the boiling point curve I shown in Figure 2. (The distillation runs were carried out with the help of low-temperature columns constructed at the Mülheim Institute [13]).

There was no characteristic break at the boiling point of isobutane (-11.8°C). Of the fractions that distilled over at -10°C to 0°C , there were small amounts of isobutene (extracted from the fraction distilled over at -10°C to 0°C and 0°C to $+10^{\circ}\text{C}$ by using 64% sulfuric acid [14a] and identified with silver nitrate solution [14b]) in addition to butane and butene.

When using active catalysts of the iron group of the periodic system which give good yields of unbranched paraffins at 180 to 250°C , mainly carbon and methane are obtained at higher temperatures. Such catalysts are unsuitable for the present studies.

When carbon monoxide and hydrogen are reacted in the presence of a catalyst of methanol synthesis in a reaction tube lined with copper, for example, then small amounts of hydrocarbons are obtained at 400 to 450°C in addition to products which contain oxygen. Curve II in Figure 1 shows the boiling point curve for a $\text{C}_3\text{-C}_4$ fraction obtained on a copper-zinc oxide catalyst. No formation of mentionable amounts of isobutane was observed. A determination of isobutene yielded 0.2 g/m^3 (STP) synthesis gas.

Curve III corresponds to the $\text{C}_3\text{-C}_4$ fraction of a hydrocarbon mixture obtained on an aluminum oxide catalyst produced by precipitation (water gas as the synthesis gas, 150 atm, 450°C). The portion of the curve corresponding to the fractions that distill over at -15°C to -5°C indicates the presence of isobutane here. The amount, based on the remaining reaction products, was small even with this catalyst, however.

Essentially different results are obtained when using thorium oxide as the catalyst. Curve IV in this figure shows that isobutane with a boiling point of -11.8°C represents a main reaction product of this synthesis. The "isosynthesis" method has been based on this new finding of the special properties of thorium oxide as a catalyst in the reaction of carbon monoxide and hydrogen. It also yields branched liquid hydrocarbons in addition to isobutane, but it yields almost no unbranched products (in contrast with the previous synthesis methods based on carbon monoxide and hydrogen).

A requirement for a satisfactory synthesis process was to eliminate wall reactions which lead to undesired byproducts. According to the results of the experiments in Table I, unlined tubes of ordinary iron could not be used at high pressures, not only for reasons of strength but also because of the undesired reactions of carbon monoxide and hydrogen which would occur at the surface. V-2-A special steel was found to be inert with respect to the synthesis gas at pressures of up to 300 atm. Extensive studies of the suitability of various metal materials for hydrogenation of carbon monoxide at 1000 atm have been carried out by Ziessecke [15].

Satisfactory results were obtained also when using iron tubes lined with copper, but aluminum was found to be an unsuitable material for the lining at high pressures, especially above 150 atm. Aluminum is destroyed by some of the oxygen-containing reaction products when the synthesis reaction is carried out at high pressures and temperatures.

A variety of methods have been tested for the production of the thorium catalysts as well as the other catalysts investigated. Catalysts produced by precipitation from dilute salt solutions have proven especially suitable. By varying the precipitation conditions, a wide range of variation in the catalyst is possible. This is also evident externally, e.g., in the apparent density, which in the case of thorium oxide was between 0.7 and 2.3, depending on the type of precipitation and pretreatment.

The normal thorium catalysts were precipitated from a solution of nitrates with soda by rapidly pouring the boiling soda solution into the boiling nitrate solution. For example, when using a concentration corresponding to 240 g thorium nitrate per 2 liters of water + 2 liters of soda solution (slight excess of sodium carbonate) this yields a hard granular catalyst with an apparent density of 1.3 after washing the precipitate until free of alkali and drying at 110°C. When concentrated solutions are used for precipitation, catalysts with a lower apparent density are obtained, e.g., a three-fold concentration yields a catalyst with an apparent density of 0.76 and an earthy to soft grain. If the precipitation is carried out very slowly, e.g., over a period of one hour, when using the concentration given for the normal catalyst, then especially dense catalysts are obtained with a vitreous break (apparent density 2.3). When precipitation is carried out with sodium hydroxide solution or ammonia, similar catalysts are obtained even when they are poured rapidly into the nitrate solution. The apparent density of the catalysts can be increased

by subsequent sintering, e.g., the catalyst designated as the normal catalyst can be increased from a density of 1.3 to 2.0 by means of an aftertreatment in an air stream at 300°C*. The dull hard grain is maintained in this process.

The catalyst dried at 110°C shrinks during the synthesis, so it is expedient to pack the largest possible amount of catalyst into a certain space and to sinter the catalyst before initial use of it or before packing it into the synthesis apparatus. Shrinkage of thorium oxide at temperatures up to 300°C is a result of the release of water and carbon dioxide. At higher temperatures, additional water that is bound by the oxide is released, but without resulting in any further sintering of the solid substance in view of the high melting point of thorium oxide (3050°C) [16]. Accordingly, there was no evidence that pretreatment at higher temperatures would cause a loss of activity of thorium oxide. On the contrary, a thorium catalyst pretreated at 1000°C in air had an especially high activity for the reaction of carbon monoxide and hydrogen. But since this catalyst had a tendency to yield somewhat larger quantities of methane, the catalysts were generally treated at 300°C.

In view of the great importance attributed to the physical nature of the catalysts as well as their chemical composition, not only with regard to the conversion but also in determining

* Alkali carbonates are precipitated from aqueous thorium solutions, releasing basic carbonate salts. $\text{ThO} \cdot \text{CO}_3 \cdot 2\text{H}_2\text{O}$ at 240°C yields [illegible]. This salt is converted to $4\text{ThO}_2 \cdot 2\text{H}_2\text{O}$ at 360°C and 2ThO_3 at even higher temperatures, especially above 400°C.

the type of reaction products, comparative studies must always be performed with catalysts that have the same history. Many different types of precipitation were tested with catalysts of varying chemical composition and the studies were always based on the best results.

The lifetime of the thorium catalyst was extremely long under the isosynthesis conditions. Catalysts which were observed to undergo an increase in internal resistance after lengthy operating times as a result of formation of carbon were restored to the original state by means of an air treatment at the synthesis temperature. In contrast with other oxides, thorium oxide can readily be regenerated with air in view of the fact that it retains its activity when heated to red heat.

In contrast with catalysts of the iron group of the periodic system, thorium catalysts are insensitive to sulfur compounds. Catalysts pretreated with hydrogen sulfide or carbon disulfide yielded normal conversion results, just as did those precipitated with ammonium sulfide.

The ratio in which the two synthesis gas components are consumed is generally about 1.2 CO to 1 H₂ in a linear gas passage (no circulation). If a synthesis gas which has a composition that corresponds to the conversion is used, higher gas yields will be obtained than when using normal water gas at a high gas conversion. However, a high carbon monoxide content more readily leads to carbon deposits, whereas when using gases with a high hydrogen content there is a greater tendency to form gaseous hydrocarbons.

III. Experiments with various single-component catalysts

Table II gives a survey of the extent to which various metal oxides (single-component catalysts) can be used as catalysts in the synthesis of hydrocarbons. The experiments on which the table is based were carried out with water gas at pressures of 30 atm, 150 atm or 300 atm at 450°C. The amount of catalyst used was 25 cm³ (bed length 30 cm) and the throughput of gas was 10 liters of end gas per hour.

The first column in the table indicates the type of catalyst used, while the second column shows the conversion of carbon monoxide and hydrogen achieved at pressure of 30, 150 and 300 atm. The third column shows the hydrocarbon content in the end gas, while the fourth column shows the average carbon number. In addition, there is a qualitative statement regarding the yield of liquid hydrocarbons, and finally the general properties of the catalyst in the synthesis reaction are described briefly.

Thorium oxide (produced as described above) is at the top of the list. As shown by the relatively high carbon numbers (2.5-2.8) it yields high-molecular-weight gaseous and liquid hydrocarbons. The gaseous hydrocarbons include large amounts of isobutane.

In the experiments conducted at 30 and 150 atm with aluminum oxide catalysts, the catalysts were produced by precipitation of the hydroxide of sodium aluminate with sulfuric acid and carbon dioxide. These catalysts were found to have a very high activity. However, they yielded mainly

methane (and carbon) in addition to small amounts of gas oil and liquid products (in accordance with the lower carbon number of the hydrocarbons of 1.4-1.5). At 30 atm the gas oil contained only traces of iso-C₄ hydrocarbons and small quantities were obtained at 150 atm. The aluminum oxide catalyst that was used for the 300 atm experiment was precipitated from dilute aluminum nitrate solution with soda in accordance with the procedure used to produce the thorium oxide catalysts and after washing was dried in a stream of air at 300°C. This catalyst proved to have a lower activity. Considerably less methane was formed than with the catalysts produced from aluminate, but there was also little production of liquid hydrocarbons and gas oil hydrocarbons (with a low isobutane content).

The tungsten catalyst was produced from sodium tungstate by precipitation with nitric acid. It had a great tendency to yield methane and carbon. There was some formation of liquid hydrocarbons.

Chromium was precipitated from the nitrate with soda. It had a low activity and yielded traces of oily products.

Titanium and beryllium proved to be inactive.

Zirconium oxide and cerium oxide were obtained from the nitrates by precipitation. They yielded liquid hydrocarbons and iso-C₄ hydrocarbons. The activity of these catalysts was lower than that of the thorium catalysts, however. The situation was similar with uranium, which was precipitated from uranyl nitrate with hydrogen peroxide.

The zinc catalysts were produced by precipitation from dilute nitrate solution with soda, but specifically in the case of the 300 atm experiment the zinc catalysts were produced by pouring the nitrate solution into the soda solution (reverse precipitation). Hardly any hydrocarbons were produced at 30 atm, but somewhat larger amounts were produced at 300 atm, although it consisted mainly of methane in addition to a very small amount of liquid hydrocarbons.

Manganese and magnesium catalysts which were also produced by precipitation from the nitrates yielded a small amount of gaseous products and traces of oily products.

Lanthanum catalysts did not yield any hydrocarbons. Praseodymium and neodymium also yielded extremely low conversions even at 300 atm.

Table III provides quantitative data on the single substance catalysts according to Table II which were found to be most suitable for synthesis of higher molecular weight hydrocarbons. These experiments were conducted at a pressure of 150 atm and a temperature of 450°C.

With thorium oxide as the catalyst, 46 vol% of the carbon monoxide-hydrogen mixture was converted, yielding 16 g isobutane* per m³ (STP) of gas used. Of the entire C₄ fraction, 83% consisted of iso-C₄ hydrocarbons. 40 g liquid hydrocarbons were also formed. Zirconium oxide was found to be somewhat less active, but was still suitable for synthesis of isohydrocarbons. With zirconium oxide as a catalyst, 32% of the carbon

* The amount of iso-C₄ hydrocarbons formed can be determined quantitatively rather rapidly by low-temperature distillation and provided a good indication here of the general suitability of the catalyst for producing branched aliphatic hydrocarbons.

monoxide-hydrogen mixture was converted and 9 g iso-C₄ hydrocarbons were obtained per m³ (STP). Here again, 82% of the C₄ fraction consisted of isohydrocarbons. The next in order of activity is cerium oxide, although it yields a considerably lower conversion. Aluminum oxide produced from sodium aluminate proved to be extremely active with regard to the CO-H₂ conversion, but only small amounts of iso-C₄ hydrocarbons and liquid products were obtained with aluminum oxide.

IV. Thorium oxide single-component catalysts

a) *Influence of reaction temperature*

Figure 3 shows a diagram of the type of reaction products obtained in isosynthesis at an operating pressure of 150 atm using thorium oxide as the catalyst and normal water gas as the synthesis gas. The operating temperatures are listed along the axis and the average composition of the reaction products is given in percentage on the ordinate.

This figure shows that the formation of alcohols is predominant in the range below actual isosynthesis, i.e., at temperatures below 400°C, but especially below 375°C, whereas at temperatures above 475°C, especially above 500°C, formation of undesired gaseous hydrocarbons such as methane, ethane and propane becomes predominant in the reactions. Between these two limits is the temperature range of isosynthesis where, for example, at 450°C (a temperature at which oxygen compounds are formed only to a very slight extent) there was a 16%

conversion to C_1 and C_2 hydrocarbons, primarily methane, 13% to C_3 and $n-C_4$ hydrocarbons, especially propane, 25% to $iso-C_4$ hydrocarbons, mainly isobutane, and 46% to liquid products, consisting primarily of branched aliphatic hydrocarbons plus a small amount of naphthenes and aromatics.

Table IV presents the number corresponding to Figure 3 for the experiments at 400°C and 450°C.

In general, a temperature near 450°C was found to be best for conducting the synthesis. The temperature limits of isosynthesis are determined by the catalyst, the operating pressure and, to a certain extent, the residence time of the gases in the reaction space.

b. *Experiments at different pressures*

Table V shows the yields obtained at a temperature of 450°C and various pressures. The gas throughput was 10 liters of end gas per 28 g thorium oxide. The yields are based on 1 m³ (STP) of CO-H₂ mixture.

The following results were obtained:

1 atm: at atmospheric pressure only a very low conversion of synthesis gas was achieved. In general, it was less than 3% of the starting carbon monoxide and hydrogen. No liquid hydrocarbons were obtained.

6 atm: About 10% of the carbon monoxide and 8% of the hydrogen were converted. In addition to gaseous hydrocarbons, small amounts of liquid products were also obtained.

30 atm: Using a water gas which contained carbon monoxide and hydrogen in a 49:41 ratio, 22% of the carbon monoxide and 21% of the hydrogen were converted. Liquid products were obtained in the amount of 14.4 g/m³ (STP), including 5.2 g iso-C₄ hydrocarbons, 5.4 g C₃ + C₄ hydrocarbons and 4.0 g C₁ + C₂ hydrocarbons. No dimethyl ether was found among the reaction products. 92% of the C₄ fraction consisted of branched hydrocarbons, 70% of which was isobutane and 30% was isobutene. The total yield of liquid plus gaseous hydrocarbons was 26.1 g.

75 atm: 31% of the carbon monoxide and 24% of the hydrogen were converted, yielding 24.4 g liquid products per m³ (STP).

150 atm: The carbon monoxide conversion was 46%, while the hydrogen conversion was 39%, yielding 36.3 g liquid hydrocarbons, 16.4 g iso-C₄ hydrocarbons, 8.3 g C₃ + n-C₄ hydrocarbons and 10.2 g C₁ + C₂ hydrocarbons. 88% of the C₄ fraction was branched and 24% of the iso-C₄ hydrocarbons were unsaturated. The total yield of liquid and gaseous hydrocarbons was 69.0 g/m³ (STP). Of the alcohols, 5.0 g were in the liquid hydrocarbons and 3.0 g were in the reaction water. The former consisted largely of isobutyl alcohol and those from the aqueous layer consisted primarily of methanol.

300 atm: Three of the experiments at 300 atm are listed in Table V. The catalyst in experiment 6 was precipitated under normal conditions, i.e., by pouring a boiling soda solution into a boiling thorium nitrate solution. The catalyst in experiment 7 was precipitated in the cold, while that in experiment 8 was produced by pouring the boiling thorium

nitrate solution into the boiling soda solution (reverse precipitation). The results were similar in all three cases. The carbon monoxide conversion was 60-65%, and the hydrogen conversion was 49-57%. 59.7 to 61.7 g liquid products were obtained, with 21.5 to 25.7 g iso-C₄ hydrocarbons, 13.2 to 17.0 g C₃ and n-C₄ hydrocarbons, 10.5 to 13.1 g C₁ and C₂ hydrocarbons. 84 to 90% of the C₄ fraction was branched and only 4 to 7% of the iso-C₄ hydrocarbons were unsaturated (in accordance with the elevated pressure). The total yields of liquid and gaseous hydrocarbons were 96.8 to 102.4 g/m³ (STP). Of the liquid products, generally 12 to 15 g consisted of alcohols, some of which were in the oil (isobutyl alcohol) and some were in the reaction water (methanol).

The amount of alcohols obtained was not always the same with different catalysts. The amount of alcohols generally increased with a lower activity, a lower apparent density and a greater age of the catalyst (also, as already pointed out, with an increase in pressure and with a reduction in temperature).

600 atm: 83% of the carbon monoxide and 70% of the hydrogen were converted, yielding 53.0 g liquid products per m³ (STP), 45.0 g iso-C₄ hydrocarbons + 22.7 g C₃ + n-C₄ hydrocarbons and 27.9 g C₁ + C₂ hydrocarbons. In addition, 5.1 g dimethyl ether were obtained and 90% of the C₄ fraction was branched. The iso-C₄ hydrocarbons consisted of 98% isobutane. The total yields of liquid products and gas oil hydrocarbons amounted to 120.7 g. The oil contained 5.3 g alcohols and the reaction water contained 3.1 g alcohols.

1000 atm: These results differ significantly from the experiments at lower pressures. About 50 g dimethyl ether and 60-70 g $C_1 + C_2$ hydrocarbons were formed per m^3 (STP). The amount of liquid products obtained was 39 g, isobutane accounted for 33 g and the $C_3 + n-C_4$ hydrocarbons constituted 12 g.

Figure 4 shows a graph for evaluation of the experiments conducted at the various pressures. This figure shows that at pressures between 300 and 600 atm, optimum conditions prevail with regard to the production of liquid products and gaseous hydrocarbons. At lower pressures, the carbon monoxide-hydrogen conversion is relatively low, and at higher pressures the formation of methane and dimethyl ether becomes predominant in the reactions. Pressures of 1000 atm or more are too high when using a thorium oxide single-component catalyst, even under different temperature conditions than in the experiments illustrated in the figure. At such pressures, temperatures lower than $450^\circ C$ lead to progressively greater formation of dimethyl ether (at $400^\circ C$ and 1000 atm, 200 g are obtained per m^3 (STP)!), while temperatures above $450^\circ C$ lead to greater production of methane. With an increase in pressure, there is an increase in the yield achieved per unit of volume of synthesis gas in a one-step process, but the temperature limits within which the formation of oxygen-containing organic compounds is no longer a problem and the formation of methane is not yet a problem tend to converge.

Table VI shows the total yields at various pressures and the percentage distribution of reaction products in the

form of liquid products, iso-C₄ hydrocarbons, C₃ + n-C₄ hydrocarbons, C₁ + C₂ hydrocarbons and dimethyl ether.

The total yield increases rather uniformly with an increase in pressure from 30.1 g/m³ (STP) at 30 atm to 200 g/m³ at 1000 atm. The percentage distribution of reaction products was always similar within a relatively wide pressure range, however.

c) *Influence of pressure and reaction time.*

The fact that the conversion of synthesis gas and thus the hydrocarbon yields increase with an increase in pressure could be interpreted as meaning that the prolonged residence time of the gases in the catalyst space, which is associated with an elevated pressure, is mainly responsible for the increase in conversion. Two series of experiments were conducted to determine whether this is in fact the case or whether a higher pressure as such is necessary for a high conversion. In the first series of experiments, the residence time of the gas was varied in a ratio of 1:2:4 by reducing the throughput using a thorium oxide single-component catalyst and the same pressure of 150 atm. In the second series of experiments, the residence time was increased while maintaining the same gas throughput by increasing the operating pressure from 150 atm to 300 or 600 atm. The results of these two series of experiments are summarized in Table VII.

Experiments 1, 2 and 3 refer to the first series of experiments and 4, 5 and 6 refer to the second series of experiments.

By reducing the amount of end gas in the first series of experiments from 10 L/hr to 5 L/hr and then to 2.5 L/hr, there was an increase in contraction values from 25% to 28% and 30%. The initial amounts calculated on this basis were, thus 13.4 L/hr, 6.95 L/hr and 3.57 L/hr. The residence times obtained from the average amounts of starting gas and end gas passing through the catalyst space per hour yielded the ratio 1:1.96:3.85. The corresponding carbon monoxide conversions were 46%, 53% and 58%. In the second series of experiments in which the pressure was raised to increase the residence time, all three experiments were carried out with a throughput of 10 liters of end gas per hour. Contraction here amounted to 29%, 37% and 51% with the corresponding initial amounts being 14.1 L/hr, 15.9 L/hr and 20.4 L/hr. The residence times yielded a ratio of 1:1.7:2.9. The carbon monoxide conversion was 46%, 65% and 83%.

A comparison of these experiments shows that at a constant pressure of 150 atm, the conversion could be increased within a certain limit by lengthening the residence time, but at higher pressures, e.g., at 600 atm, the carbon monoxide conversion was considerably greater than at lower pressures, despite the shorter residence time of the gases in the catalyst space. See, for example, experiments 3 and 6. In terms of weight, the conversion of carbon monoxide at 600 atm was 8 times greater than that at 150 atm. The increased gas conversion observed by increasing the synthesis pressure is thus considerably greater than can be achieved by lengthening the residence time of the gases in the catalyst space.

Although the type of reaction products is similar within a wide pressure range (see Table VI), working at low pressures and accordingly longer residence times of the synthesis gas in the catalyst space is no substitute for the necessity of working at high synthesis pressures in order to achieve high CO-H₂ conversion.

This also corresponds to the fact (presumably based on the equilibrium conditions in a primary reaction) that at atmospheric pressure there is hardly any CO-H₂ conversion even when the gas throughput is extremely low (e.g., when the gas throughput is reduced to 1/30th of the usual amount).

d) *Performing the synthesis in stages and with circulation*

First, 2 synthesis ovens were operated in a "single stage", working with a normal ThO₂ catalyst at a pressure of 150 atm and a temperature of 450°C. The synthesis gas contained 43.1% carbon monoxide and 48.6% hydrogen. The hourly throughput of synthesis gas per 28 g ThO₂ over a long period of operation was 11.4 L/hr with oven I and 13.7 liters per hour with oven II. The two synthesis ovens did not function completely the same. The contraction amounted to 28% and 27%, CO conversion was 55% and 50%, and the CO-H₂ consumption ratios were 1.29:1 and 1.20:1. The ratio of the amount of carbon dioxide formed (in addition to the hydrocarbons) to the reaction water (in moles) was 3.42:1 and 3.77:1. A comparison of these two experiments with experiment 1 in Table VII shows that the catalysts used in the experiments in Table VIIIa had a somewhat higher activity. But otherwise the conditions were the same.

In the third experiment in Table VIIIa, synthesis ovens I and II were connected in series. Since the amount of gas entering oven I was not increased, the synthesis gas throughput per 28 g ThO_2 dropped to 1/2, namely to 6.0 L/hr. Between ovens I and II, the liquefied products were separated at a synthesis pressure of 150 atm and a temperature of -25°C . The total contraction achieved in ovens I and II now amounted to 45% and the CO conversion was 75%. When this "two-step experiment" is compared with experiment 2 in Table VII, where the gas throughput per quantity of catalyst was approximately the same, it may be noted that conversion is considerably higher in the two-step process (with intermediate separation of reaction products) than with the one-step experiment with the same average gas load of the catalyst. In accordance with the fact that the gaseous CO and H_2 entering the second synthesis step no longer has a ratio of 43.1:48.6, but instead now has a ratio of 24.7:40.9, i.e., it has a higher hydrogen content, the CO/H_2 consumption ratio of the total mixture is shifted toward the hydrogen side and the ratio of the formation of carbon dioxide to water is shifted toward the water side.

Table VIIIb lists the hydrocarbon yields of the two one-step experiments and Table VIIIa gives the results of the two-step experiment. The total yields were 72.9, 67.9, and 111.3 g, the liquid products constituted 45.2 wt%, 49.8 wt% and 35.6 wt%, the iso- C_4 hydrocarbons constituted 25.8 wt%, 27.8 wt% and 32.4 wt%. In accordance with the increased hydrogen consumption of the two-step process, the amount of gaseous hydrocarbons obtained in this process was also

somewhat greater than in the one-step process. When the findings presented in Table VIIIb are compared with those in Table VI, it can be seen that approximately the same total yields are achieved in the two-step synthesis process at 150 atm as in the one-step process at 300 atm with approximately the same average residence time of the gases in the catalyst space. However, the throughput of synthesis gas by weight was about twice as high per unit of time and unit of catalyst at 300 atm as at 150 atm.

In another two-step experiment conducted at 150 atm, where a CO-richer synthesis gas (48.6% CO and 41.7% H₂) was used and the two steps were not carried out at the same temperature (first step 430°C, second step 470°C), so the conversions could be evenly distributed between both ovens, a total of 125.7 hydrocarbons were obtained (37.6% liquid products, 26.8% iso-C₄ hydrocarbons).

In addition to the "stepped experiments" so-called "circulation experiments" were also carried out, where the synthesis gases were passed repeatedly over the same catalyst in accordance with the diagram in Figure 5, each time removing the liquid reaction products and some of the gas oil by cooling the circulating gas to ca. -25°C under pressure. A substream was removed as the end gas after the condensation system and a corresponding amount of fresh synthesis gas was fed into the circuit before the synthesis oven. The amount of gas leaving the system amounted to about 10 L/hr per 28 g ThO₂, as in the normal experiments. The pumping ratio, i.e., the ratio of the amount of fresh gas feed to the circulating

gas, was 1:6. Tables IXa and IXb show the results of such an experiment conducted at 30 atm as well as a comparative experiment which was carried out in the same contact apparatus without pumping the synthesis gas in circulation. With a linear passage of the gas, the contraction amounted to 20.5%, CO conversion was 40% and the CO-H₂ consumption ratio was 1.14:1, but in the circulating process contraction was 29%, CO conversion was 32.4% and the CO-H₂ consumption ratio was 0.67:1. In other words, the CO consumption is lower in the circulating process and the H₂ consumption and degree of liquefaction are higher than in the normal method of carrying out the synthesis in one stage. This corresponds to the larger production of "reaction water" in the circulating process. However, the aqueous phase may still contain methanol, as subsequent experiments indicated. This question was not investigated at that time, however. The total yields of hydrocarbons (see Table IXb) are about the same with and without pump circulation, but the amount of liquid product is greater with the circulation process, possibly due to an increased alcohol content. Although the stepped experiments with intermediate removal of reaction products thus offer the possibility of extensive CO workup at moderate pressures, the circulating process is an easy method of varying the workup ratio of carbon monoxide and hydrogen in a relatively wide range.

In additional publications to appear soon, further catalyst developments will be discussed along with extensive analytical tests and engine tests of the isosynthesis products.

Summary

"Isosynthesis," a new method of hydrocarbon synthesis, is described. This involves high-pressure hydrogenation of carbon monoxide at pressures of more than 30 atm, especially between 300 and 600 atm, and temperatures of 450°C. Thorium oxide was found to be the best single-component catalyst. Other catalysts that are suitable include ZrO_2 , CeO_2 and, although it is far less effective, Al_2O_3 . Gaseous and liquid hydrocarbons are formed, with the C_4 hydrocarbons consisting of 80 to 90% branched compounds, for example.

If the pressures are too high (more than 600 atm) and the temperatures are too low (less than 400°C), significant amounts of oxygen-containing compounds are formed (especially methanol, isobutanol and dimethyl ether).

At 600 atm and 450°C, a yield of about 15.4 g is obtained from 1 m³ (STP) CO-H₂ mixture on a ThO₂ catalyst. This yield consists of 34.5% liquid products, 29.3% iso-C₄ hydrocarbons, 14.7% C₃ and n-C₄ hydrocarbons and 18.2% C₁ + C₂ hydrocarbons, plus 3.3% dimethyl ether.

By working in several stages, the yield can be increased significantly at moderate pressures. With a circulating process, the CO/H₂ workup ratio can be shifted largely toward the hydrogen consumption side.

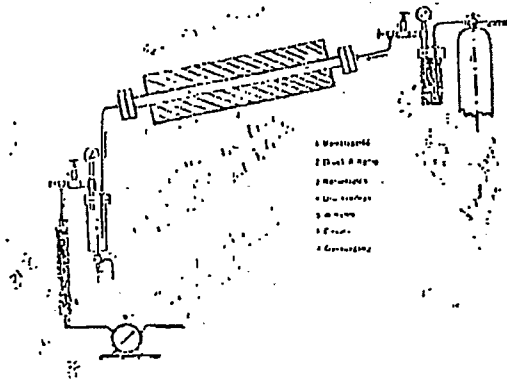


Figure 1. Pressurized apparatus for isosynthesis.

- Key:
- 1. Storage vessel
 - 2. Pressurized vessel containing activated carbon
 - 3. Contact oven
 - 4. Pressurized receiving vessel
 - 5. Activated carbon
 - 6. Gas meter
 - 7. Gas outlet

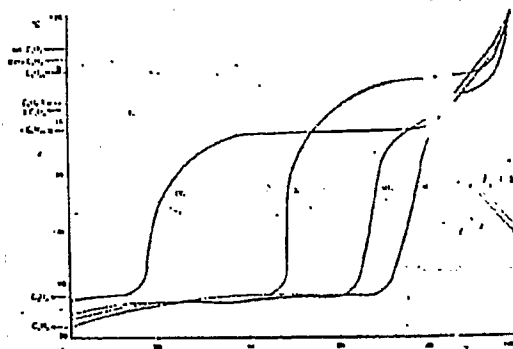


Figure 2. Low-temperature distillation of C₃-C₄ fractions obtained on various catalysts.

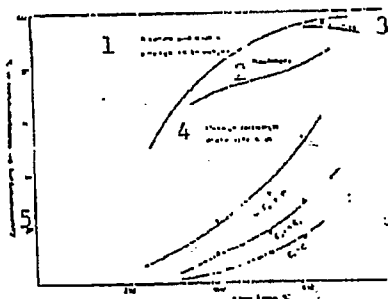


Figure 3. Isosynthesis (150 atm). Composition of the reaction products as a function of temperature using a ThO₂ single-component catalyst.

- Key:
1. Alcohols and other oxygen-containing compounds
 2. Naphthenes
 3. Aromatics
 4. Liquid branched aliphatic hydrocarbons
 5. Composition of the reaction products in %

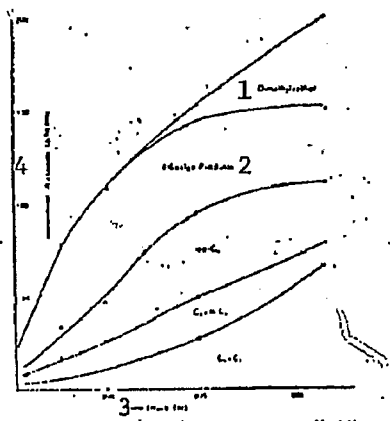


Figure 4. Influence of pressure on the amount and type of the reaction products of isosynthesis (ThO_2 single-component catalyst, 450°C).

- Key:
1. Dimethyl ether
 2. Liquid products
 3. Pressure
 4. Yield (g/m^3)

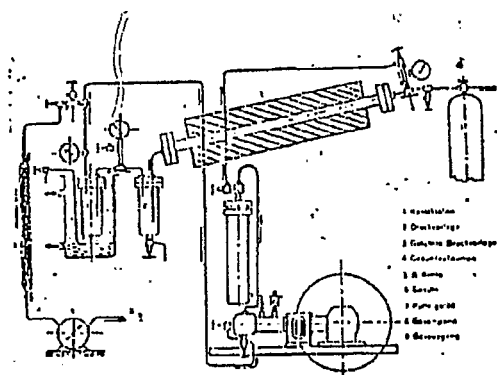


Figure 5. Pressurized apparatus for circulating experiments.

- Key:
1. Contact oven
 2. Pressurized receiving vessel
 3. Cooled pressurized receiving vessel
 4. Gas circulating pump
 5. Activated carbon
 6. Gas meter
 7. Buffer vessel
 8. Gas inlet
 9. Gas outlet

Table I. Conversion of water gas in an empty unalloyed steel tube (450°C, 30 atm).

	CO ₂	H ₂ O	H ₂	CO	H ₂	C ₂ H ₄	C ₃ H ₈	C ₄	N ₂
4 Anfangsgas.....	0,8	0,0	0,2	11,1	10,0	1,0	1,1	7,0	
5 Reaktionsgas nach 1 Tag....	0,4	0,7	0,1	6,4	10,1	1,2	1,2	14,1	
6 Reakt. n. 30 Tagen	12,8	0,5	0,2	0,4	20,7	22,0	1,2	11,8	

- Key: 1. Heavy hydrocarbons
 2. Hydrocarbons
 3. No. of carbons
 4. Starting gas
 5. ~~Reaction gas after one day~~
 6. Reaction gas after 30 days

Table III. The properties of various catalysts, with special emphasis on the iso-C₄ hydrocarbons.

Catalysator	1. Vol% um- gewandelt	2. iso-C ₄ in g/m ³ (STP) reines Gas	3. % iso-C ₄ in der Gesamtc ₄ -Fraktion	4. Öl + Gasoline in g/m ³ (STP) reines Gas
PtO ₂	16	16	88	40
ZnO ₂	32	9	84	—
Co ₂	10	1,3	81	—
Al ₂ O ₃	51	2,8	50	5

- Key:
1. Catalyst
 2. Vol% converted gas
 3. iso-C₄ in g/m³ (STP) pure gas
 4. % iso-C₄ in the total C₄ fraction
 5. Oil + gasoline in g/m³ (STP) pure gas

Table IV. Isosynthesis on a ThO₂ single-component catalyst at 400°C and 450°C and 150 atm.

Temperatur	Ausbeute in g Nebenfraktion						3. flüssige Produkte*
1.	C ₂	C ₃	C ₄	n-C ₄	iso-C ₄	5.	6.
400	2,9	0,2	1,6	1,1	7,1	5,7	—
450	2,5	2,5	7,8	1,9	16,4	21,6	—

* für die Bestimmung der flüssigen Reaktionsprodukte sind in einem besonderen Abschnitt Erwähnung.

- Key:
1. Temperature, °C
 2. Yield in g/m³ (STP) pure gas
 3. Liquid products*
 4. * The test for "liquid reaction products" is discussed in a separate section.

Table V. Experiments with ThO₂ as catalyst at various pressures (450°C).

1	2	3	4	5	6	7							12	13	14	15
						8	9	10	11	12	13	14				
1	1	ThO ₂ normal	49:41	2.1	2.1	—	1.0	1.1	—	—	—	—	1.2	1.3	1.4	1.5
2	6	ThO ₂ normal	41:49	—	4.0	—	—	—	—	—	—	—	—	—	—	—
3	20	ThO ₂ normal	49:41	22	21	15.4	0.4	0	5.2	5.1	4.0	0	0.2	30	20.1	
4	75	ThO ₂ normal	49:41	31	21	23.1	—	—	—	—	—	—	—	—	—	
5	150	ThO ₂ normal	49:41	61	39	36.3	5.0	5.0	16.4	8.3	10.0	—	0.5	4	0.1	
6	300	ThO ₂ normal	49:41	65	51	51.7	—	—	23.4	13.2	13.4	—	—	—	—	
7	300	ThO ₂ with 1% oil	43:43	63	51	45.2	5.1	9.4	25.7	17.0	—	—	—	8.1	7	
8	300	ThO ₂ with 2% oil	41:49	64	49	41.7	7.6	12.1	21.5	13.7	10.0	—	—	—	—	
9	481	ThO ₂ normal	40:50	64	70	44.0	5.4	3.1	45.0	22.7	27.0	5.1	—	—	—	
10	1041	ThO ₂ normal	44:47	61	—	—	—	—	—	—	—	—	—	—	—	

- Key:
1. Experiment No.
 2. Pressure, atm
 3. Catalyst
 4. Synthesis gas CO:H₂
 5. CO conversion (%)
 6. H₂ conversion (%)
 7. Yields in g/m³ (STP) pure gas
 8. Liquid hydrocarbons
 9. Alcohols
 10. In the oil
 11. In the H₂O
 12. Dimethyl ether
 13. iso-C₄ hydrocarbons in the total C₄ hydrocarbons
 14. % iso-C₄H₈ of the total iso-C₄ hydrocarbons
 15. Liquid products + gas oil in g/m³ (STP) pure gas
 16. Precipitated cold
 17. Reverse precipitation

Table VI. Yields at various pressures of % of the total reaction products (450°C).

1. Druck at	2. Gesamt- ausbeute g/g Ethol	3. Gew. % der Gesamtfraktion					5.
		H ₂ Prod.	C ₂	C ₂ +n-C ₄	C ₃ +C ₄	D. Ä.	
30	30,1 ⁴	52,5	17,3	10,9	13,1	5	
150	70,2*	50,0	20,7	10,4	12,9	4	
300	109,1	50,5	20,8	12,1	16,5	..	
450	151,7	34,5	23,1	14,7	16,2	3,3	
1100	261	19,5	16,5	0,0	21,5	24,5	

- Key:
1. Pressure (atm)
 2. Total yield in g/m³ (STP)
 3. Amount of the total yield in wt%
 4. Liquid products
 5. Dimethyl ether

Table VII. Experiments at various residence times of the synthesis gas in the reaction space.

Nr.	Druck at	Endgas L/hr	Contra- ktion %	Anf. Gas (g/hr)	statist. An- haltzeit (min)	Avg. Res. time s
1	150	10	25	13,3	normal	34
2	150	5	28	6,65	1,96-fach	53
3	150	2,5	30	3,32	1,85-fach	58
4	150	10	20	14,1	normal	40
5	300	10	37	15,9	1,7-fach*	65
6	1100	10	51	20,1	2,9-fach*	83

*) Nach Berücksichtigung der Abweichungen des prozentwertes bei hohen Drücken.

- Key:
1. No.
 2. Pressure
 3. End gas, L/hr
 4. Contraction (%)
 5. Starting gas, L/hr
 6. Average residence time
 7. CO conversion in %
 8. Times
 9. * Taking into account the deviations in pv value at higher pressures

Table VIIIa. Step experiments (ThO₂ catalyst; CO:H₂ = 43.1:48.6, 150 atm, 450°C).

Synth. oven	Vol. gas L/hr per 28 g ThO ₂	Contraction %	CO conversion %	CO:H ₂ Verh. nach	g/H ₂ min		Σ C _n H _m
					CO	H ₂	
I	11,3	28	53	1,20:1	206	21,0	3,42:1
II	14,7	27	59	1,2:1	194	21,0	3,77:1
I+II	0,0	45	73	1,05:1	265	43,0	4,37:1

- Key:
1. Synthesis oven
 2. Starting gas, L/hr per 28 g ThO₂
 3. Contraction (%)
 4. CO conversion (%)
 5. CO:H₂ consumption ratio
 6. g/m³ (STP)

Table VIIIb. Step experiments (ThO₂ catalyst; CO:H₂ = 43.1:48.6; 150 atm, 450°C).

Synth. oven	Gesamtfl. fl. W. g/Stunde	Σ Gew.-% der Gesamtflüssigkeit	Gew.-% der Gesamtflüssigkeit		
			1-C ₁	C ₂ +nC ₂	C ₃ +C ₄
I	72,0	35,2	23,8	11,5	14,5
II	67,0	49,8	27,8	11,2	11,4
I+II	111,3	35,0	32,4	14,4	11,2

- Key:
1. Synthesis oven
 2. Total hydrocarbons, g/m² (STP)
 3. Portion of total yield in wt%
 4. Liquid products

Table IXa. Circulating experiment (ThO₂ catalyst, CO:H₂ = 43.3:48.0, 30 atm, 475°C).

1	2	3	4	5
6 ohne	11.4	20.5	50	1.11:1
mit 7	12.4	29	32.4	0.07:1

- Key:
1. Pump circulation
 2. Starting gas, L/hr 28 g ThO₂
 3. Contraction (%)
 4. CO conversion (%)
 5. [illegible]
 6. Without
 7. With

Table IXb. Circulating experiment (ThO₂ catalyst, CO:H₂ = 43.3:48.0, 30 atm, 475°C).

1	2	3	4	5	6
6 ohne	31.9	22	18.7	25.1	34.6
mit 7	32.6	39.8	20.4	19.2	18.8

- Key:
1. Pump circulation
 2. Total hydrocarbon yield in g/m³ (STP) reaction gas
 3. Portion of total yield in wt%
 4. Liquid products
 5. And
 6. Without
 7. With

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