

# THE ISOSYNTHESIS<sup>1</sup>

By

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## Preface

By N. GOLUMBIC

THIS bulletin is a translation of a German manuscript describing an investigation of the synthesis of branched-chain hydrocarbons that was carried out in the laboratories of the Kaiser Wilhelm Institute for Coal Research under the direction of Helmut Pichler. The paper contains data on the development of the catalyst for the isosynthesis, on the effect of temperature and pressure of operation, and on the composition of the products of the reaction. In the last section, experimental evidence

and speculations concerning the mechanism of the isosynthesis are discussed.

The organization of the manuscript was revised in the technical editing process in order to present the material somewhat more concisely. The major part of this revision consisted in rearrangement of the tables and figures to combine related data and elimination of long descriptions of the data summarized in tabular form.

## Introduction

High-quality fuels, particularly aviation fuels, must satisfy certain requirements. Specifications relate to the boiling range of the fuel, its purity, its stability in storage and in cold weather, and its suitable resistance to ignition by compression, that is, high octane rating.<sup>5</sup> The most satisfactory compounds are the isoparaffin hydrocarbons, whose resistance toward ignition by compression increases with the density of the molecular structure and is particularly high for those compounds that contain one or more tertiary or, preferably, quaternary carbon atoms. Until recently, Germany lacked the necessary raw materials to prepare isoparaffins in sufficient quantity.<sup>6</sup> Aromatic compounds, obtained as byproducts in the coking process and as products of high-pressure hydrogenation of coal, also have high octane ratings, which also are largely independent of the boiling point of the individual hydrocarbons. However, aromatic compounds have a marked tendency to form soot. The antiknock ratings of naphthenes

and olefins that boil below 100° C. are satisfactory for numerous purposes. Unsaturated hydrocarbons, however, do not make satisfactory aviation fuels. n-Paraffins, which are liquid at ordinary temperatures, are known to have antiknock ratings, the quality of the fuel declining as the molecular chain increases.

The effect on the octane rating of the addition of lead tetraethyl is greatest for paraffins, somewhat less for naphthenes, and least for aromatics. The behavior of olefins in this respect varies with their structure. Aromatic compounds with relatively long, saturated, aliphatic side chains tend to behave in the same way as paraffins.

Iso-butene and iso-butane are known to be important starting materials in the production of high-quality aviation gasolines. For example, polymerization of iso-butene followed by hydrogenation,<sup>7</sup> or alkylation of iso-butane,

<sup>1</sup> Egloff, G., *Polymer Gasoline: Ind. and Eng. Chem.*, vol. 28, 1936, pp. 1461-1467.

<sup>2</sup> Heinze, R., *Öl, Kohle, Erdöl, u. Teer*, vol. 12, 1936, p. 185.

<sup>3</sup> Ipatieff, V. N., *Catalytic Polymerization of Gaseous Olefins by Liquid Phosphoric Acid. I. Propylene: Ind. and Eng. Chem.*, vol. 27, 1935, pp. 1067-1069.

<sup>4</sup> Ipatieff, V. N., and Pines, H., *Polymerizing Butylene to Form Gasoline Hydrocarbons: U. S. Patent 2,181,942 (1939)*.

<sup>5</sup> Standard Alcohol Co., *Polymerizing Olefins: Brit. Pat. 456,315 (1936)*;

*French Pat. 806,611 (1936)*.

<sup>6</sup> Standard Oil Development Co. and I. G. Farben., *Brit. Pat. 457,158 (1936)*;

*French Pat. 822,790 (1937)*.

<sup>7</sup> Standard Oil Development Co., *French Pats. 827, 123, 849, 047 (1937)*;

*835, 051, (1938)*.

<sup>8</sup> Wagner, C. R., *Production of Gasoline by Polymerization of Olefins: Ind. and Eng. Chem.*, vol. 27, 1935, pp. 933-936.

<sup>1</sup> Work on this manuscript completed June 1949.

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<sup>4</sup> Research chemist, Office of Synthetic Liquid Fuels, Research and Development Branch, Bureau of Mines, Pittsburgh, Pa.

<sup>5</sup> Marder, M., [*Motor Fuels*]: Verlag Springer, Berlin, 1942, p. 459.

<sup>6</sup> Egloff, G., [*Modern Hydrocarbon Syntheses*]: Brennstoff Chem., vol. 18, 1937, pp. 115-117.

<sup>7</sup> Ipatieff, V. N., *Catalysis in the Mineral-Oil Industry: Petroleum*, vol. 33, No. 45, 1937, pp. 1-5.

with a compound such as n-butene,<sup>8</sup> produces the valuable aviation fuel iso-octane. In the current processes for the synthesis of liquid fuels from coal, only relatively small amounts of iso-C<sub>4</sub>-hydrocarbons are produced. The amounts obtained by high-pressure hydrogenation of coal by the Bergius-I. G. Farbenindustrie A. G.<sup>9</sup> process vary with operating conditions. Normal-pressure synthesis<sup>10</sup> (Fischer-Tropsch<sup>11</sup>) and medium-pressure synthesis (Fischer-Pichler<sup>12</sup>), both of which have been applied on an industrial scale by the Ruhrchemie A. G.,<sup>13</sup> yield 0.5 to 1 percent of iso-C<sub>4</sub>-hydrocarbons based on the total amount of reaction products.

In addition, except for a few organic chemistry laboratory methods and the polymerization of olefins, iso-hydrocarbons are prepared either by catalytic isomerization or by splitting n-paraffins in the presence of aluminum halides.<sup>14</sup> Iso-butene may also be obtained from iso-butyl alcohol, which, in turn, is obtained by synthesis from carbon monoxide and hydrogen in the presence of zinc catalysts. However, the main product of this process is methanol, iso-butyl alcohol representing only about 20 to 30 weight percent of the liquid reaction products.<sup>15</sup>

To date, no process exists in which coal or its gasification products are used as starting materials in preparing isoparaffins. The devel-

opment of such a process, known as the "isosynthesis," was the purpose of the present work. As in the synthesis of n-paraffins, the starting materials are carbon monoxide and hydrogen. The isosynthesis differs from the other processes, which are catalyzed by elements belonging to the iron group of the periodic systems, in that it makes use particularly of thorium oxide as catalyst. The operating temperature and pressure are high, and consequently the reaction follows an entirely different course.

in the normal pressure synthesis over cobalt catalysts. In the saturated C<sub>7</sub>-fraction, 7.5 percent of isobutane was obtained. Precise distillation of the C<sub>7</sub>-C<sub>8</sub> fraction showed that the normal paraffins n-pentane, n-hexane, and n-heptane predominated. Small amounts of singly-branched hydrocarbons, such as methylbutane, 2-methylpentane, 3-methylpentane, 2-methylhexane, and 3-methylhexane were present. Multi-branched paraffins were present only in traces, if at all. U. von Weber (Angew. Chem., vol. 57, 1939, p. 607) reported that the branching number (mol fraction) of hexane is 0.15, heptane 0.20, octane 0.27, nonane 0.35, and decane 0.40. In this synthesis, a tertiary carbon atom is present for every 25 to 50 carbon atoms, whereas quaternary carbon atoms are present in only minute quantities, if at all.

<sup>8</sup> Fischer, F., [Synthesis of Motor Fuel (Kogasin) and Lubricating Oil from CO and H<sub>2</sub> at Atmospheric Pressure]: Brennstoff Chem., vol. 10, 1935, pp. 1-11.

Fischer, F., [Review of the Syntheses Using CO and H<sub>2</sub>]: Brennstoff Chem., vol. 24, 1943, pp. 517-522.

<sup>12</sup> Fischer, F., and Pichler, H., [Synthesis of Paraffin Hydrocarbons from CO and H<sub>2</sub> over Cobalt Catalysts (Medium-Pressure Synthesis)]: Brennstoff Chem., vol. 20, 1939, pp. 41-43.

Fischer, F., and Pichler, H., [Approximation of the Possible Theoretical Yields in the Fischer-Pichler Medium-Pressure Synthesis]: Brennstoff Chem., vol. 20, 1939, pp. 221-228.

<sup>13</sup> Martin, F., [The Development of the Synthesis of Hydrocarbons from Water Gas]: Chem. Fabr., vol. 12, 1939, pp. 233-240.

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<sup>14</sup> Calingaert, G., and Flood, D. T., The Isomerization of Normal Heptane: Jour. Am. Chem. Soc., vol. 57, 1935, p. 956.

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<sup>15</sup> Natta, G., and Rigamonti, R., [The Synthesis of Aliphatic Alcohols by the Catalytic Reduction of Carbon Monoxide]: Giorn. Chim. Ind. applicata, vol. 14, 1932, pp. 217-225.

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<sup>8</sup> Birch, S. F., Pim, F. B., and Tait, T., High Anti-Knock Fuels from Lower Olefins: Jour. Soc. Chem. Ind., vol. 55, 535-537T (1936).

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<sup>9</sup> Pier, M., [Hydrogenated Benzines (Gasolines). Influence of Raw Material, Catalyst, and Processing Method]: Angew. Chem., vol. 51, 1933, pp. 603-608.

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<sup>10</sup> An extensive investigation was made by H. Koch and F. Hilberath [Hydrocarbons Boiling Below 100° C. in Synthetic Gasoline from Carbon Monoxide and Hydrogen (Kogasin)]: Brennstoff Chem., vol. 22, 1941, pp. 135-139, 145-152) of the -100° C. hydrocarbon fraction produced

## EXPERIMENTAL PART

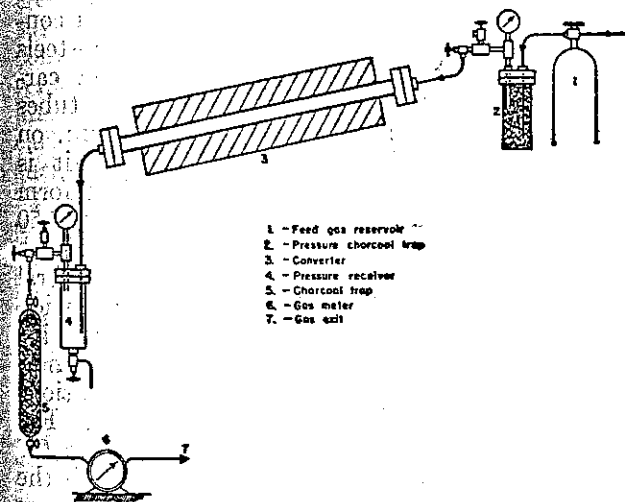
### APPARATUS

The experimental apparatus shown diagrammatically in figure 1 consisted of the following:

A. 1,000-atmosphere Andreas Hofer compressor.

B. A high-pressure storage chamber for pressures up to 1,000 atmospheres, consisting of a high-pressure Krupp tube 275 millimeters i. d. and 3.5 meters long, closed by stoppers screwed in at each end. To avoid carbonyl formation and prevent seepage at the stoppers, the tube was fitted in the workshop of the Institute with a brass lining.

C. A battery of six steel flasks placed between the high-pressure storage chamber and the converter at pressures below 350 atmospheres to insure constant pressure.



- 1 - Feed gas reservoir
- 2 - Pressure charcoal trap
- 3 - Converter
- 4 - Pressure receiver
- 5 - Charcoal trap
- 6 - Gas meter
- 7 - Gas exit

FIGURE 1.—SCHEMATIC DIAGRAM OF ISOSYNTHESIS APPARATUS

D. The reactor, consisting of a pressure tube, either lined with copper or made of carbon monoxide-resistant steel, placed in a metal aluminum block.

E. A trap in which the major part of the liquid reaction products was collected under pressure and whose temperature was kept above 31° C. to prevent carbon dioxide from liquefying.

F. Activated charcoal trap in which the low-boiling liquid reaction products and gasol were removed from the outlet gas.

The amount of inlet gas was determined by measuring the outlet gas, reduced to atmos-

pheric pressure, and calculating the contraction values from the difference in nitrogen values for the inlet and outlet gas. The composition of the gasol hydrocarbons was determined by low-temperature distillation, and that of the liquid hydrocarbons by careful fractional distillation, generally after preliminary mild hydrogenation.

Refractive indexes, densities, etc., were determined for the individual hydrocarbon fractions. The antiknock ratings of the distilled and stabilized crude and hydrogenated gasoline fraction were determined by the motor method (I. G. testing engine) both before and after addition of lead tetraethyl.

### PRELIMINARY TESTS

When water gas is passed at 20 liters per hour through an empty unalloyed-steel tube (12 millimeters i. d., 400 millimeters heater length) at 30-atmospheres pressure and 450° C., a reaction takes place between carbon monoxide and hydrogen to give as principal products

TABLE 1.—Conversion of water gas in an empty, unalloyed, steel tube at 450° C. and 30 atmospheres

Gas	Time, days	Gas composition, percent by volume							
		CO <sub>2</sub>	Ole-fins	O <sub>2</sub>	CO	H <sub>2</sub>	Hydro-carbons	C-No.	N <sub>2</sub>
In-gas.....	0	0.8	0	0.2	44.1	46.9	1.0	1.1	7.0
Reaction gas.....	1	34.4	0.7	.1	6.4	13.1	31.2	1.23	14.1
Do.....	30	32.8	.5	.2	9.1	23.3	22.6	1.25	11.8

carbon, carbon dioxide, and low-boiling hydrocarbons, especially methane.

Table 1 shows the composition of the inlet and outlet gas obtained in a 30-day experiment of this type. Hydrocarbon homologues of methane are formed in small amounts, as shown by the carbon numbers for saturated hydrocarbons. The calculated yield was 8.5 grams of C<sub>3</sub> hydrocarbons, 7.4 grams of C<sub>4</sub> hydrocarbons, and 2 grams of gasoline per cubic meter of water gas. During synthesis, carbon deposits form in the tube and gas conversion gradually decreases.

Low-temperature distillation of the C<sub>3</sub>-C<sub>4</sub> fraction gave the boiling-point curve shown in figure 2, curve I. Distillations of this type were carried out with a low-temperature column

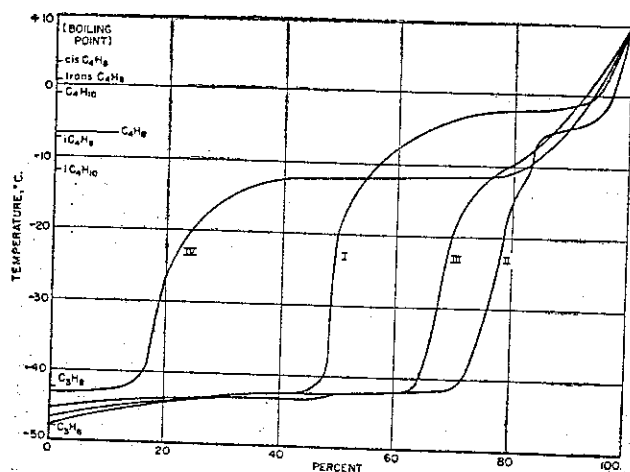


FIGURE 2.—LOW-TEMPERATURE DISTILLATION OF  $C_3$ - $C_4$  FRACTIONS FROM VARIOUS CATALYSTS.

constructed in the Mülheim Institute.<sup>16 17</sup> The curve shows no characteristic break at the boiling point of iso-butane ( $-11.8^\circ\text{C}$ ). The fractions distilling between  $-10^\circ$  and  $0^\circ\text{C}$ . contained n-butane, n-butene, and small amounts of iso-butene. The latter was extracted with 64 percent sulfuric acid from the fractions distilling between  $-10^\circ$  and  $0^\circ\text{C}$ . and between  $0^\circ$  and  $10^\circ\text{C}$ .<sup>18</sup> The mercury nitrate test also was used<sup>19</sup> for identification.

Active iron-identification catalysts, which give good yields of straight-chain paraffins between  $180^\circ$  and  $300^\circ\text{C}$ ., produce mainly carbon and methane when operated at higher temperatures. Such catalysts cannot be used in the isosynthesis. When carbon monoxide and hydrogen react in a copper-lined converter at  $400^\circ$  to  $450^\circ\text{C}$ . in the presence of a catalyst ordinarily used in synthesizing methanol, small amounts of hydrocarbons are formed in addition to oxygenated compounds. Curve II, figure 2, represents the boiling-point curve of the  $C_3$ - $C_4$  fraction obtained with a copper-zinc oxide catalyst. No appreciable amount of iso-butane was observed. The iso-butane yield was found to be 0.2 gram per cubic meter of synthesis gas.

Curve III, figure 2, was obtained for the  $C_3$ - $C_4$  fraction of a hydrocarbon mixture

<sup>16</sup> Fischer, F., and Weinrotter, F., [Production of Gaseous Olefinic Hydrocarbons by Thermal Decomposition of Kogasin]: Brennstoff Chem., vol. 21, 1940, pp. 215-217.

<sup>17</sup> Koch, H., and Hilberath, F., [Apparatus for Low-Temperature Fractional Distillation]: Brennstoff Chem., vol. 21, 1940, pp. 197-203.

<sup>18</sup> Dobrjanski, Refer. Chem. Ztrbl., vol. 1926, I, p. 2220.

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<sup>19</sup> Hurd, C. D., and Pilgrim, F. D., The Pyrolysis of Hydrocarbons. Further Studies on the Butanes: Jour. Am. Chem. Soc., vol. 55, 1933, pp. 4902-4907.

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obtained with a precipitated alumina catalyst (water gas, 150 atmospheres,  $450^\circ\text{C}$ .). The portion of the curve corresponding to the fractions distilling between  $-15^\circ$  and  $-5^\circ\text{C}$ . shows evidence of the presence of iso-butane. However, the amount was small.

The results were completely different when thoria was used as catalyst. Curve IV, figure 2, showed iso-butane to be one of the principal reaction products. This specific behavior of thoria constitutes the basis of the isosynthesis. In addition to iso-butane, liquid branched hydrocarbons also were produced; the yield of straight-chain compounds was negligible.

The elimination of undesirable side reactions at the surface of the tube proved to be essential. As observed in table 1, unlined tubes of ordinary iron are unsuitable for use at high pressures because of the reactions that take place at their surface between carbon monoxide and hydrogen. V-2-A-extra steel was found to be inert toward water gas at high pressures. Of various steels tested by passing synthesis gas over shavings of the metal at 250 to 300 atmospheres and  $460^\circ\text{C}$ ., those with a high chromium content apparently were inert; lower-grade steels produced carbon dioxide, methane, iron carbonyl, and carbon. Copper-lined iron tubes also gave satisfactory results. Aluminum, on the other hand, was not suitable, as it is attacked by oxygenated compounds that form during synthesis at high pressure (above 150 atmospheres).

The catalysts were prepared by several methods. Catalysts obtained by precipitation from dilute salt solutions were found to give particularly good results. Changing the conditions produced a wide variety of preparations that differed even in external properties. For example, the bulk density varied between 0.7 and 2.3, according to the method by which the catalyst was precipitated and the preliminary treatment to which it was subjected.

The standard thorium catalyst was prepared by rapidly pouring a boiling sodium carbonate solution into a boiling thorium nitrate solution. The precipitate was then washed free from alkali and dried at  $110^\circ\text{C}$ . When 240 grams of thorium nitrate in 2 liters of water was precipitated by 2 liters of carbonate solution (slight excess of sodium carbonate), a hard granular catalyst was obtained whose bulk density was 1.3. If precipitation was carried out with more concentrated solutions, the catalysts had a lower bulk density. Thus, when the concentration of the solution was tripled, the catalyst had a bulk density of 0.76, and its granule had a soft, earthy consistency. When the standard concentration was used, but precipitation was carried out very slowly (for example, over a period of 1 hour), the

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resulting catalyst was a heavy, glasslike substance. Catalysts of this type (bulk density 2.3) formed even upon rapid precipitation when sodium hydroxide or ammonia was used as precipitant. The bulk density could also be increased by subsequent sintering in a current of air. Thus, treatment of a standard catalyst in air at 300° C. increased its bulk density from 1.3 to 2.0.<sup>20</sup> In this case, the dull, hard granule persisted.

Catalysts dried at 110° C. were observed to shrink during synthesis. As it is desirable for a given catalyst volume to contain a maximum weight of catalyst, the catalyst should be sintered before being operated or, preferably, before being charged into the converter. Up to 300° C., the shrinkage of thorium oxide is due to a loss of water and carbon dioxide. At higher temperatures, the oxide still gives off water, but, owing to the high melting point of thorium oxide (3,050° C.), there is no further sintering of solid material.<sup>21</sup> Accordingly, there is no reason to believe that preliminary treatment of thorium oxide at higher temperatures affects its catalytic activity. On the contrary, a thorium compound treated in a current of air at 1,000° C. was found to be particularly active in catalyzing the conversion of carbon monoxide and hydrogen. However, as such catalysts showed a tendency to promote

methane formation, pretreatment at 300° C. was adopted as standard.

When operated under the conditions of the isosynthesis, thorium catalysts were found to have a remarkably long life. In cases where prolonged operation led to an increased pressure drop across the catalyst bed because of the formation of carbon, it was found that the catalyst could be restored to its original activity by treating with air at the synthesis temperature. Thorium oxide differs from other oxides in that it can be heated to red heat without loss in activity and that, as a result, it can be satisfactorily regenerated with air.

In contrast to catalysts belonging to the iron group of the periodic system, thorium catalysts are unaffected by sulfur compounds. Neither preliminary treatment with hydrogen sulfide or carbon disulfide nor precipitation with ammonium sulfide had any effect upon the normal degree of conversion.

For a single pass of synthesis gas (without recycle), the usage ratio of CO:H<sub>2</sub> is generally about 1.2:1. When the composition of the synthesis gas is the same as the usage ratio, higher gas conversion and, consequently, higher yields are obtained than when ordinary water gas is used. A further increase in the carbon monoxide content of the gas favors carbon formation, whereas hydrogen-rich gas favors gaseous hydrocarbons.

#### EXPERIMENTS WITH VARIOUS ONE-COMPONENT CATALYSTS

Table 2 contains a summary of the results obtained with various metal oxides (one-

TABLE 2.—Effect of one-component oxide catalysts in the isosynthesis (450° C., 25 cc. catalyst, 10 l. end gas/hour)

Catalyst	Starting material	Percent gas conversion at—			Hydrocarbons in end gas, percent	C-No.	Oil	Remarks
		30 atmos.	150 atmos.	300 atmos.				
ThO <sub>2</sub>	Nitrate	19			2.1	2.5	+	Gasol contains much isobutane; uniform activity.
ThO <sub>2</sub>	do		46		5.1	2.6	+	Do.
ThO <sub>2</sub>	do			66	6.4	2.8	+	Do.
Al <sub>2</sub> O <sub>3</sub>	Na aluminate	54			11.0	1.4	+	Traces of iso-C <sub>4</sub> , much CH <sub>4</sub> and carbon.
Al <sub>2</sub> O <sub>3</sub>	do		53		10.5	1.5	+	Some iso-C <sub>4</sub> , much CH <sub>4</sub> and carbon.
Al <sub>2</sub> O <sub>3</sub>	Al nitrate			21	3.1	2.0	+	Little iso-C <sub>4</sub> .
Cr <sub>2</sub> O <sub>3</sub>	Na tungstate+HNO <sub>3</sub>	58			12.9	1.3	+	Much methane and carbon.
TiO <sub>2</sub>	Nitrate	19			3.0	1.5	+	Traces.
BeO		0				0	0	
ZrO <sub>2</sub>	Nitrate	9			1.0		+	Poor conversion.
ZrO <sub>2</sub>	do		31		3.5	2.1	+	Iso-C <sub>4</sub> , very little carbon.
ZrO <sub>2</sub>	do			36	3.5	2.3	+	Do.
UO <sub>2</sub>	Nitrate and H <sub>2</sub> O <sub>2</sub> <sup>1</sup>				3.7	1.4	+	Do.
ZnO	Nitrate	10			1.2	1.3	+	Traces.
ZnO	Nitrate <sup>2</sup>			44	10.0	1.1	+	Very little hydrocarbon.
MnO	Nitrate				1.2	1.3	+	Little liquid hydrocarbon.
MgO	do	15			.8	1.2	+	Very little hydrocarbon.
CeO <sub>2</sub>	do	12			3.0	1.3	+	Traces.
CeO <sub>2</sub>	do	7			.5	2.0	+	Traces.
La	do	3	10		1.0	2.4	+	Traces.
La	do							Little iso-C <sub>4</sub> .

<sup>1</sup> 21 percent at 75 atmospheres.

<sup>2</sup> Inverse precipitation: Nitrate added to sodium carbonate solution.

component catalysts). The experiments were carried out with water gas at pressures of 30, 150, and 300 atmospheres and at 450° C. The charge of catalyst was 25 cc. (length of layer, 30 centimeters) and the throughput 10 liters of outlet gas per hour.

The relatively high carbon number of the gaseous hydrocarbons (2.5–2.8) obtained in the presence of thoria shows that, in addition to liquid hydrocarbons, this catalyst produced the higher molecular-weight gaseous hydrocarbons. The gaseous hydrocarbons include large amounts of iso-butane.

The aluminum oxide catalysts used in the experiments at 30 and 150 atmospheres were prepared by precipitating the hydroxide with sulfuric acid or carbon dioxide from a sodium aluminate solution. These catalysts produced principally methane and carbon, together with small amounts of gasol and liquid compounds (see low carbon number, 1.4–1.5). Only traces

TABLE 3.—Production of iso-C<sub>4</sub> hydrocarbons in the presence of several 1-component catalysts

Catalyst	Gas conversion, volume percent	i-C <sub>4</sub> , g./m <sup>3</sup> gas <sup>a</sup>	i-C <sub>4</sub> , percent in total C <sub>4</sub> fraction	C <sub>3</sub> + hydrocarbons, g./m <sup>3</sup> gas <sup>a</sup>
ThO <sub>2</sub> .....	46	16	88	40
ZrO <sub>2</sub> .....	32	9	82	.....
CeO <sub>2</sub> .....	10	1.3	81	.....
Al <sub>2</sub> O <sub>3</sub> <sup>b</sup> .....	53	2.8	59	5

<sup>a</sup> G./m<sup>3</sup> inert-free feed gas.

<sup>b</sup> Prepared from sodium aluminate.

of iso-C<sub>4</sub> hydrocarbons were present in the gasol formed at 30 atmospheres. The product obtained at 150 atmospheres contained slightly larger amounts of these compounds. The aluminum oxide catalyst used in the 300-atmospheres experiment was prepared by the same general method as the thorium oxide catalyst. A dilute solution of aluminum nitrate was precipitated with sodium carbonate. The precipitate was washed and dried in a current of air at 300° C. This catalyst showed little activity.

Table 3 contains the quantitative data for those oxides that were found to be best suited for use as one-component catalysts in the isosynthesis. The catalysts were, in order of their effectiveness, the oxides of thorium, zirconium, cerium, and aluminum.

## THORIA ONE-COMPONENT CATALYST

### EFFECT OF SYNTHESIS TEMPERATURE

Figure 3 shows graphically the types of reaction products obtained by isosynthesis with water gas over a thorium oxide catalyst at an operating pressure of 150 atmospheres. The

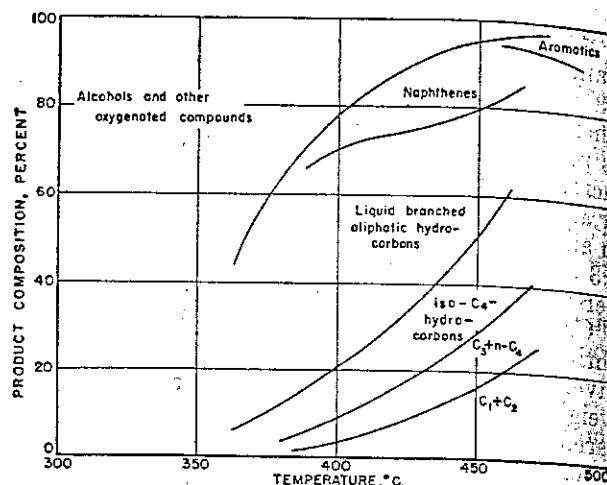


Figure 3.—COMPOSITION OF PRODUCTS OF THE ISOSYNTHESIS OBTAINED OVER THORIA CATALYST AT 150 ATMOSPHERES

operating temperatures are shown on the abscissa and the average percent composition of the reaction products on the ordinate. Alcohol formation predominates at temperatures below that of the isosynthesis, that is, below 400° C., and especially below 375° C.; whereas, at temperatures above 475° C., and particularly above 500° C., methane, ethane, and propane are the principal products. The temperature region for the isosynthesis lies between these two limits. At 450° C., for instance, a temperature at which formation of oxygenated compounds is low, the graph shows 16 percent of methane and small amounts of C<sub>2</sub> hydrocarbons; 13 percent of C<sub>3</sub> and n-C<sub>4</sub> hydrocarbons, chiefly propane; 25 percent of iso-C<sub>4</sub> hydrocarbons, with iso-butane predominating; and 46 percent of liquid compounds, primarily branched aliphatic hydrocarbons and smaller amounts of naphthenes and aromatics. Table 4 summarizes some of the data in figure 3.

### EFFECT OF SYNTHESIS PRESSURE

Table 5 and figure 4 show the effect of pressure upon the liquid and gasol yields at 450° C.

It will be noted that best results were obtained at pressures of 300 to 600 atmospheres. Below 300 atmospheres, carbon monoxide-hy-

TABLE 4.—Isosynthesis in the presence of a ThO<sub>2</sub> catalyst (150 atmospheres)

Temperature, °C.	Yields, g./m <sup>3</sup> gas <sup>a</sup>					
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	n-C <sub>4</sub>	i-C <sub>4</sub>	C <sub>3</sub> +
400.....	2.9	0.2	2.6	1.1	7.3	48.7
450.....	9.5	2.5	7.8	1.9	18.4	34.6

<sup>a</sup> G./m<sup>3</sup> inert-free feed gas.

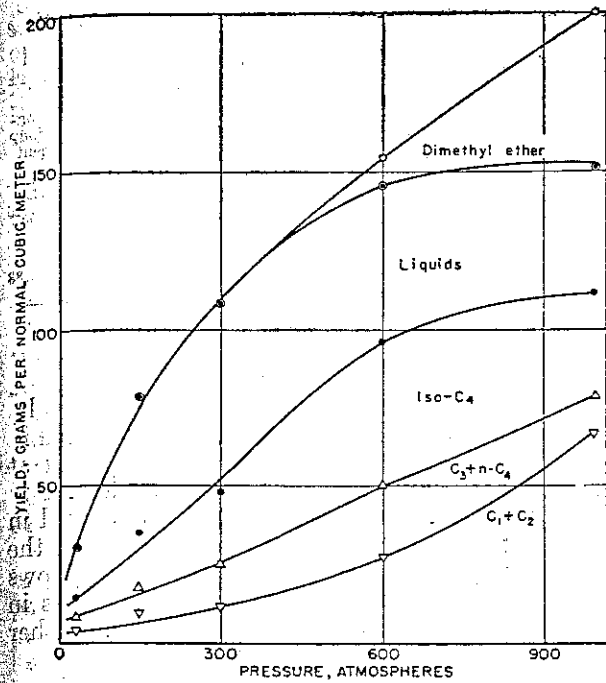


FIGURE 4.—INFLUENCE OF PRESSURE UPON THE NATURE AND QUANTITY OF THE PRODUCTS OF THE ISOSYNTHESIS ( $\text{ThO}_2$  CATALYST,  $450^\circ \text{C}$ .)

drogen conversion was relatively small. Above 600 atmospheres, methane and dimethyl ether were the principal products. At 1,000 atmospheres, there was observed a decrease in isobutane and total yield and a sharp increase in dimethyl ether. Pressures of 1,000 atmospheres and above are too high to be used with thorium oxide catalyst, even under other temperature conditions. At such pressures, temperatures below  $450^\circ \text{C}$ . produced sizable quantities of dimethyl ether (at  $400^\circ \text{C}$ . and 1,000 atmospheres, 200 grams per cubic meter gas). Temperatures above  $450^\circ \text{C}$ . produced much methane. As the pressure increased, the yields obtained per unit volume of synthesis gas (single-stage process) increased, but the temperature range in which oxygenated organic compounds no longer form, and methane formation is not yet appreciable, was small.

The last five columns of table 5 show that the total yield increased with increase in pressures, and that the distribution of the reaction products remained fairly constant over a wide range of pressures. At 1,000 atmospheres, 60 percent of the total yield consisted of  $\text{C}_1$  and  $\text{C}_2$  hydrocarbons and dimethyl ether.

TABLE 5.—Effect of pressure on isosynthesis over  $\text{ThO}_2$  catalyst ( $450^\circ \text{C}$ ., 10 l. end gas/28 g.  $\text{ThO}_2/\text{hr}$ .)

Experiment No.	Pressure, atmospheric, absolute	$\text{ThO}_2^a$ catalyst	S. G. <sup>b</sup> CO: $\text{H}_2$	Conversion, percent		Yields, g./Nm <sup>3</sup> ideal gas				
				CO	$\text{H}_2$	$\text{C}_2^+$ H. C. <sup>c</sup>	Liquids		Total	
							Oil	$\text{H}_2\text{O}$		
1	0	A	49:41	<3	<3					
2 <sup>d</sup>	6	A	43:48	~10	~28					
3	30	A	49:41	22	21	15.0	0.4	0		15.4
4	75	A	49:41	31	24					24.4
5	150	A	49:41	46	39	36.3	5.0	3.0		44.3
6	300	A	49:41	65	57					61.7
7	300	B	45:45	60	51	45.2	5.1	9.4		59.7
8	300	C	41:49	61	49	41.7	7.6	12.3		61.6
9	600	A	40:50	83	70	44.6	5.3	3.1		53.0
10	1,000	A	44:47	90						39.0

Experiment No.	Yields, g./Nm <sup>3</sup> ideal gas—Continued						Product distribution, weight percent of total yield						
	Gases				Total liquids plus gasol	Total yield	i-C <sub>4</sub> , percent of C <sub>4</sub>	i-C <sub>4</sub> H <sub>8</sub> , percent of i-C <sub>4</sub>	Liquids	i-C <sub>4</sub>	$\text{C}_2^+$ n-C <sub>4</sub>	$\text{C}_1+\text{C}_2$	Di-Me-ether
	i-C <sub>4</sub>	$\text{C}_2^+$ n-C <sub>4</sub>	$\text{C}_1+\text{C}_2$	Di-Me-ether									
1													
2 <sup>d</sup>													
3	5.2	5.1	4.0	0	25.7	29.7	92	30	52.0	17.4	17.2	13.4	0
4				0	69.0	79.2	88	24	56.0	20.7	10.4	12.9	0
5	16.4	8.3	10.2		98.3	111.4	85	4	55.4	21.0	11.8	11.8	
6	23.4	13.2	13.1		102.4		84	7					
7	25.7	17.0			96.8	106.8	90	5	57.6	20.1	12.8	9.5	
8	21.5	18.7	10.0		120.7	153.7	90	2	34.5	29.3	14.8	18.1	3.3
9	45.0	22.7	27.9	5.1	84.0	200.0	90		19.5	16.5	6.0	33.5	
10	33.0	12.0	67.0	49.0									

<sup>a</sup> A=normal catalyst; B=catalyst precipitated at room temperature; C=catalyst prepared by inverse precipitation.  
<sup>b</sup> S. G.=synthesis gas.  
<sup>c</sup> H. C.=hydrocarbons.

<sup>d</sup> Small amounts of liquid and gaseous hydrocarbons produced.  
<sup>e</sup> Chiefly isobutyl alcohol.  
<sup>f</sup> Chiefly methanol.