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Procedure for the Catalytic Conversion
of Carbon Monoxide and Hydrogen to Hydrocarbons.

December 18, 1942.

Translated by W. Oppenheimer

Hitherto, it was not possible to produce, by direct conversion from CO and H₂, hydrocarbons which have antiknock characteristics necessary for airplane fuel. By a roundabout way, the unbranched or the singly-branched aliphatic hydrocarbons with a relatively low octane number, which originates in the hydrogenation of carbon monoxide, were subsequently treated by aromatization, isomerization, or alkylation.

A new conversion process was found, by which it is possible to produce from CO and H₂ liquid antiknock hydrocarbons as isobutane, which is the starting material for high-grade airplane fuel. The operation works with raised pressure and temperatures above 350°C., preferably above 450°C., but below 600°C. (that means below a point where a disturbing formation of carbon begins), and with a thorium catalyst. With higher pressure, the conversion of CO increases and the temperatures may be kept somewhat lower than with lower pressure. The herein described process operates with thorium compounds, preferably thorium oxide, which are, if necessary, fixed on a carrier. The range of pressure, and temperature where a conversion of gas takes place is:

10 atmospheres, 480° to 600°C.
100 atmospheres, 425° to 600°C.
1000 atmospheres, 350° to 600°C.

The range of the best operation for a one-stage throughput is essentially:

10 atmospheres, 500° to 550°C.
100 atmospheres, 450° to 550°C.
1000 atmospheres, 400° to 550°C.

The range, which covers the invention, is best illustrated in Figure 1.

The thorium catalysts are advantageously prepared by precipitation of thorium salt solutions, and it is useful on occasion to add as a carrier material broken unglazed clay or silica gel, or for dilution, kieselguhr. It is necessary for a high yield of valuable hydrocarbons to operate as far as possible without the presence of elements of the iron group in the periodic table.

Under the prevailing conditions, vanadium, chromium, and molybdenum are not as troublesome as the metals of the iron group, but with increasing addition, they are responsible for the formation of carbon. Besides this, with increasing addition of these elements, the yield of branched hydrocarbons decreases fast. With temperatures around 500°C., only small amounts of aromatics remain besides the reaction products of carbon and gaseous hydrocarbons.

Increasing additions of manganese, especially when 10 percent or more is added, also changes the kind of reaction products. The total yield of liquid hydrocarbons decreases gradually; and instead of branched hydrocarbons, cyclic substances, smelling like terpenes, or with temperatures around 500°C., although with small yield, almost pure aromatic hydrocarbons are formed.

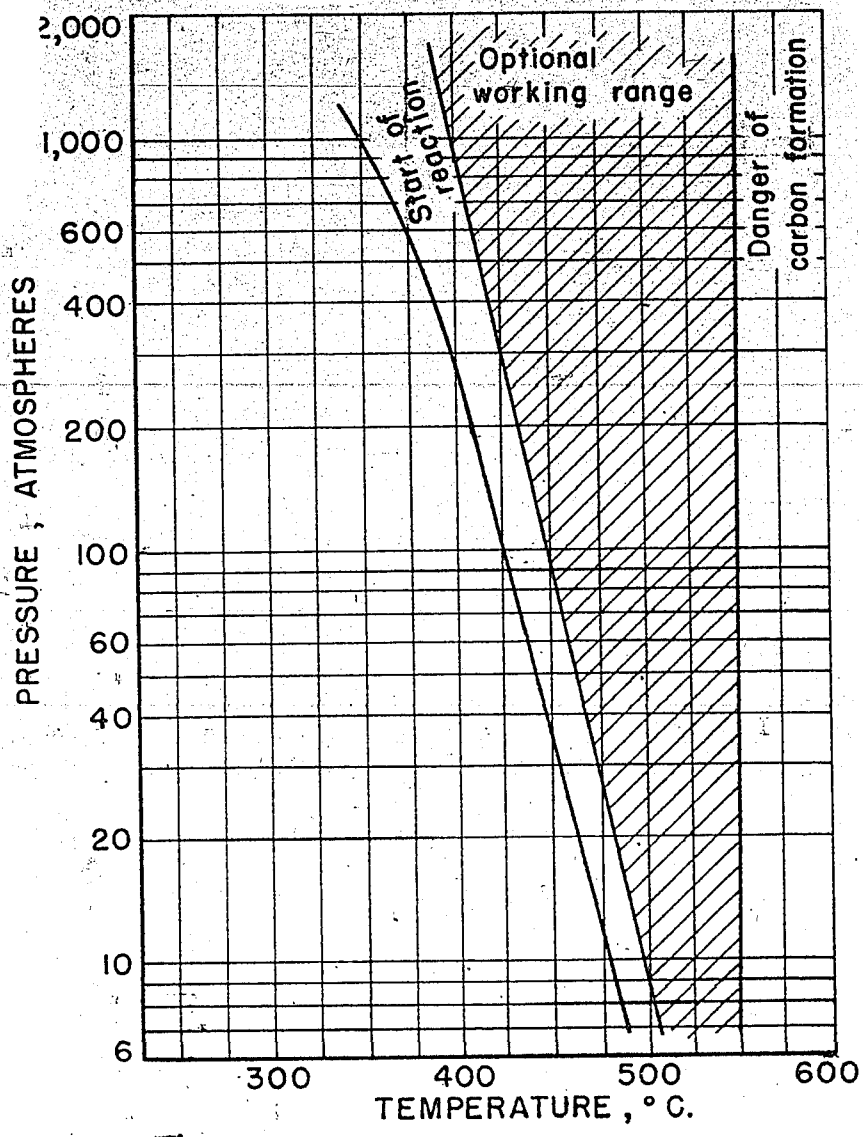


Figure 1. -

One paper exists which concerns the hydrogenation of carbon monoxide with thorium-manganese as catalyst (Ges. Abh. z. Kenntn. Kohle, 12, 296). A pressure of 30 atmospheres at 450°C. was used. Only small amounts of unsaturated and methane hydrocarbons (C number = 1) were obtained, which corresponds to the above statement on manganese. Otherwise, it is stated that "a somewhat watery condensate, smelling like hydroaromatic compounds" was formed. From this experimental result, therefore, no useful process for the catalytic conversion, in the sense of the present invention, could be derived. The present process would have required higher temperatures at a pressure of 30 atmospheres. Besides that, as mentioned before, an addition of larger amounts of manganese to the catalyst had to be avoided.

Processes for the production of antiknock motor fuel have been suggested before. However, they are being run in two stages. In the first stage, oxygen-containing substances are produced on catalysts which are known for the conversion of the higher alcohols. The portions boiling up to 110°-115°C. are transformed by splitting off water and by polymerization and hydrogenation into branched hydrocarbons. Only then, the higher-boiling portions are converted by direct hydrogenation into the corresponding hydrocarbons.

The serviceable catalyst for the first stage of the known process have to be metal oxides of the second, third, fifth, sixth, or seventh group of the periodic table, and they must contain at least one element of the first group. Thorium and all other metals of the fourth group of the periodic table are explicitly excluded.

By means of our invention, contrary to the known suggestion, the antiknock branched hydrocarbons shall be made in one operation. Surprisingly, the thorium, an element of the fourth group in the periodic table and rejected in the known project, proved to be a specific catalyst which cannot be replaced by the catalysts recommended in the known project, and which may be useful in the conversion of alcohols.

The present process, on the whole, has nothing to do with experiments in which in the first stage, hydrocarbons are formed which are refined in a second stage under different conditions and are then polymerized, isomerized, and aromatized.

On the other hand, it is advantageous, under certain conditions of the present process, to run the conversion in several stages. However, the reaction products in this case are, after each stage, completely or partially removed and are in this way protected against further conversion. Such a method results in an increasing yield of valuable higher hydrocarbons and a decreasing amount of methane. This object can also be reached by a recycle method by which the gases are passed over the same catalyst with high velocity. Each time the converted products, after leaving the reacting zone, are completely or partially removed from the reaction gas.

Example

(1) The catalyst was made from a diluted thorium nitrate solution by precipitating with sodium carbonate. After washing, drying, and granulating the catalyst, 450 grams of this catalyst were equally distributed in 16 copper-lined pipes of 30 cm. length and 1 cm. width, built into a reaction apparatus. A gas containing 50 percent carbon

monoxide and 40 percent hydrogen with a pressure of 40 atmospheres was used. 175 liters per hour (referred to 1 atmosphere) passed through the apparatus at a temperature of 500°C. In one stage, one-third of the CO and H₂ was used up. 100 Grams gasoline and gasol (C₃+C₁₁) hydrocarbons besides methane and C₂ hydrocarbons were formed per cubic meter. The gasoline, which contained predominantly branched-aliphatic hydrocarbons besides naphthenes and aromatics, had an olefin content of 15 percent, a refractive index $n_D^{20} = 1.40$, and, according to the boiling range an octane (motor method) number 80 - 90. Two-thirds of the C₄-gasol fraction consisted of isobutane. The catalyst retained its constant efficiency for several months.

(2) The same catalyst, the same gas, the same throughput, and the same temperature were used as in (1), but with a pressure of 150 atmospheres. In one stage, two-thirds of the carbon monoxide-hydrogen mixture were used up and 150 grams liquid and gasol (C₃+C₁₁) hydrocarbons were formed. This is about three times as much per cubic meter gas used, as with 40 atmospheres pressure.

(3) The same catalyst, the same gas, the same throughput were used as in (1) and (2), but, with a pressure of 1000 atmospheres and a temperature of 450°C., 85 percent of the CO and the H₂ had been converted. However, the liquid reaction products, in contrast to the operation with lower pressures contained 20 percent water-soluble organic compounds.

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Patent Claims.

(1) The herein described process for the catalytic production of hydrocarbons, such as isobutane from CO and H₂, is operated with thorium compounds, preferably thorium oxide which, if necessary, are fixed on a carrier. The range of pressure and temperature where a conversion of gases takes place is:

10 atmospheres, 480° to 600°C.
100 atmospheres, 425° to 600°C.
1000 atmospheres, 350° to 600°C.

(2) The herein described process, according to Claim (1), and a conversion with the range of pressure and temperature of:

10 atmospheres, 500° to 550°C.
100 atmospheres, 450° to 550°C.
1000 atmospheres, 400° to 550°C.

(3) The herein described process, according to Claims (1) and (2), and the use of a thorium catalyst, which is prepared by precipitation from thorium salt solutions.

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