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Process for the Production  
of Antiknock Hydrocarbons.

Translated by W. Oppenheimer

Hitherto, processes for the catalytic conversion of CO and H<sub>2</sub> under high pressure and temperature, for example, a pressure up to 1000 atmospheres and over and temperatures from 200° to 600°C. are known. 10,000 Liters and more gas per hour per one-liter catalyst are converted. The resulting reaction products usually consist of oxygen-containing compounds, such as alcohols, chiefly methanol. It has been proposed before to produce, by catalytic conversion of CO and H<sub>2</sub> with thorium oxide antiknock hydrocarbons (Applications for patent, St 61225 Ivd/120 and St 62438 Ivd/120). In these unpublished applications, for example, with thorium oxide (produced by precipitation), with temperatures from 400° to 500°C., and a pressure up to 1000 atmospheres, and an hourly throughput of gas, which was the 400- to 1000-fold of the catalyst volume, up to 150 grams mostly valuable branched hydrocarbons per normal cubic meter. CO-H<sub>2</sub> mixtures have been obtained.

This method has one disadvantage, the scarcity of the catalyst substance.

A part of the thorium or even the whole thorium, it was discovered, may be replaced by other compounds of (1) elements of the third to the sixth group (2) of the period table, which cause dehydration, for example, by aluminum oxide, tungsten oxide, zirconium oxide, or by rare earths. In case the operation is run under a higher pressure, for example, with aluminum oxide or with zirconium oxide and a pressure of 150 atmospheres, similar yields could be obtained as with thorium oxide and 30 atmospheres.

The present invention came from the perception that for certain catalysts, which must contain a dehydration-causing constituent, a temperature limit exists. Below this limit, preferably oxygen-containing compounds are formed; and above it, hydrocarbons of special antiknock value result.

According to this invention for the production of anti-knock hydrocarbons and branched aliphatic hydrocarbons by catalytic conversion of CO and  $H_2$ , we propose to operate with high pressure and high temperature and to use, instead of or beside thorium oxide, compounds which cause dehydration. Catalysts of this kind are oxides of elements of the third to the sixth group of the periodic table, especially aluminum oxide, tungsten oxide, zirconium oxide, uranium oxide, or rare earths. The pressure for this operation has to be above 100 atmospheres, preferably between 200 to 500 atmospheres or higher, the temperature for each catalyst has to be above the range of a predominant formation of methanol or dimethyl ether.

The temperatures of the operation, which are above the range of a predominant formation of oxygen-containing organic compounds, are always over  $350^\circ$ , preferably over  $400^\circ C$ . At these tem-

peratures under the conditions of the present conversion, preferably branched aliphatic hydrocarbons are formed. With still higher temperatures, the quantity of cyclic hydrocarbons increase, that is, first naphthenes and then aromatics occur.

It became further evident, that much better yields of anti-knock hydrocarbons could be obtained when to the said catalysts, a compound like zinc oxide was added, which at lower temperature favors the formation of methanol. It is advantageous to have a surplus by weight of the dehydrating catalyst for example aluminum oxide, tungsten oxide, etc., over the one which favors the formation of methanol (zinc oxide). In this manner, the formation of hydrocarbons instead of oxygen-containing organic compounds was promoted, and the application of too high a temperature which could form larger amounts of cyclic compounds was prevented.

A very high yield of hydrocarbons is obtained if the catalysts are precipitated together, for example, aluminum and zinc with sodium carbonate from a solution of nitrates, or with carbon dioxide or even sulfuric acid from a solution of aluminate and zincate.

#### Example

For the operation with an aluminum-oxide:zinc oxide catalyst (1:1) prepared by precipitation, the best conditions are a pressure of 300 atmospheres, a flow rate of 400 liters per hour and per liter catalyst, and a temperature of 410°C. as limiting temperature, below which mostly alcohol is formed.

At 300 atmospheres and under the conditions of the above experiment, that is, the same composition and activity of the catalyst, the same flow velocity of the gas, etc., and a water-gas tem-

perature around  $410^{\circ}\text{C}$ ., 100 grams gasol and liquid hydrocarbons per normal cubic meter inert-free out gas were produced. The liquid hydrocarbons consisted for the most part of branched aliphatic hydrocarbons; 80 percent of the  $\text{C}_4$  fraction was isobutane + isobutene.

Patent Claims.

1. The herein described process for the production of anti-knock hydrocarbons and branched aliphatic hydrocarbons by catalytic conversion of  $\text{CO}$  and  $\text{H}_2$  under high pressure and temperature operates with dehydrating catalysts of the third to the sixth group of the periodic table, especially aluminum oxide, tungsten oxide, zirconium oxide, uranium oxide, or rare earth instead of a thorium catalyst.

The pressure has to be above 100 atmospheres, preferably from 200 to 500 atmospheres and over, and the temperatures, which have to be established for each catalyst, must be above the range of a predominant formation of methanol and dimethyl ether.

2. The herein described process, according to Claim 1, is operated by increasing the activity of the catalysts by addition of elements preferably zinc oxide, which at lower temperatures than the temperature of the conversion, favor the formation of methanol.

3. The herein described process, according to Claims 1 or 2, is operated by the application of a surplus of those catalysts which have a dehydrating action.

4. The herein described process, according to Claim 1, 2, or 3, is operated with a catalyst mixture produced by the co-precipitation of the different catalysts.

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