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PATENT SPECIFICATION

2254

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(Under Section 91, Subsections (2) and (4) (a) of the Patents and Designs Acts, 1907 to 1932, a single Complete Specification was left in respect of this Application and of Applications Nos. 33361/37, 33362/37, and was laid open to inspection on June 3, 1938.)

COMPLETE SPECIFICATION

Process for the Catalytic Production of Hydrocarbons

We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, a Corporation organised under the Laws of Germany, of 45, Bockenheimer Anlage, Frankfurt-on-the-Main, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the catalytic production of hydrocarbons.

The catalytic conversion of gases containing carbon monoxide and hydrogen into liquid hydrocarbons of higher molecular weight with several linkages chiefly of the olefine and paraffin type, is carried out with so-called synthesis gases in which the ratio of carbon monoxide to hydrogen is 1:2. It is customary to produce—for the Fischer-Tropsch benzine-synthesis process under ordinary pressure (see Brennstoffchemie, 1935, No. 1, pp. 1—11) —a synthesis gas which contains up to 30% of carbon monoxide and 58 to 60% of hydrogen, the remainder consisting of about 10 to 12% of inert gases (CO_2, N_2 and CH_4) so-called because they take no part in the reaction.

Experiments have also been performed with diluted synthesis gases in which a degree of dilution—referred to a 100% mixture of carbon monoxide and hydrogen—of 20 to 40% is obtained by the addition of nitrogen, methane and carbon dioxide (see "Journal of the Society of Chemical Industry, Japan," Vol. 37, No. 11, pp. 704-716B). The yields of liquid products obtained in these experiments, and expressed in cubic centimetres per cubic metre of the synthesis gas, are inferior to those from a high-percentage synthesis gas with the usual $CO:H_2$ ratio of 1:2. In fact it was found that the extensively diluted gases have a very unfavourable effect on the benzine synthesis, and that progressive dilution of the originating gas is accompanied by the production of a gradually more volatile and lighter synthetic benzine (loc. cit. p. 711 B).

Various attempts have also been made to perform the benzine synthesis under elevated pressure (for example, 5 to 10 atmospheres) with the known synthesis gas containing only up to about 15% of inert gas constituents. In so doing, however, such extensive amounts of high-boiling products were formed, which choked the pores of the catalyst to such an extent that the activity of the contact mass was speedily destroyed. Experiments of this kind are described in "Brennstoffchemie," Vol. 12, No. 19, pp. 365—372, and Vol. 14 (1933), No. 1, pp. 3—8. Although the catalyst remains active for a longer period when the reaction temperature is raised, undesirable water-soluble products—especially alcohols and acids—are formed which destroy the apparatus and render the practicability of the whole process problematical.

It has now been ascertained that good results can be obtained in the conversion of gases containing carbon monoxide and hydrogen, into liquid hydrocarbons, with the aid of the known catalysts employed in the Fischer-Tropsch benzine-synthesis, (i.e. a catalyst suitable for the formation of benzine, oil, and paraffin at atmospheric pressure and at a temperature of between 150° and 265° C. i.e. below that at which methane would normally be exclusively formed) by carrying out the process under superatmospheric pressure with a dilute synthesis gas, separating at least part of the hydrocarbons formed by the catalytic conversion from the end gas of the synthesis and recycling a part of said end gas through the same catalytic conversion and supplying to one or more points of the synthesis apparatus beyond the point of admission of said end-gas, fresh synthesis gas rich in carbon monoxide and hydrogen.

Based on the foregoing discovery, the present invention provides a process for the catalytic conversion of gases containing carbon monoxide and hydrogen, into hydrocarbons containing more than two carbon-atoms in the molecule with the aid

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of catalysts, as hereinbefore defined, at temperatures between 150° and 265° C. which process comprises supplying to the contact furnace a diluted synthesis gas, applying a superatmospheric pressure in said contact furnace of above 2 atmospheres separating at least a part of the hydrocarbons formed by the said catalytic conversion from the end gas, recycling a part of the end gas to the inlet of the contact furnace, and admitting fresh gas rich in carbon monoxide and hydrogen beyond the point of admission of the recycled end gas, such that the gas undergoing the catalytic conversion always contains more than 20% of inert constituents (such as CO_2, CH_4, N_2).

In the catalytic conversion of mixtures of carbon monoxide and hydrogen into valuable organic compounds containing more than 1 carbon atom in the molecule, from such gas mixtures of carbon monoxide and hydrogen as are free from or low in extraneous gases not taking part in the reaction and which contain the carbon monoxide and hydrogen in the requisite proportions for the synthesis, it has already been proposed to carry out the operation in a circulatory system and to introduce such extraneous gases into the mixture of carbon monoxide and hydrogen either previously to, or at the commencement of, and if desired, also during the reaction, so that the circulating gases always contain at least 40% by volume of extraneous gases whilst the fresh gases admitted into the cycle consist of a mixture of carbon monoxide and hydrogen, substantially free from extraneous gases. According to the foregoing proposal moreover, the lowering of the partial pressure of carbon monoxide and hydrogen by the admixture of extraneous gases may be counteracted by raising the total pressure, pressures of for example, 20 to 1000 or more atmospheres being used.

A suitable catalyst which may be employed in carrying out the invention consists for example of cobalt, thorium oxide and kieselguhr and may be composed of 33% of cobalt, 5% of thorium oxide and 61% of kieselguhr.

In certain cases, it may be advisable to add to the dilute recycled gas, further diluents such as CO_2, H_2O, alcohols, higher hydrocarbons, and so forth. It is also of advantage to employ, as diluents, substances (for example, CH_4, CO_2, and the like) which occur, in the reaction, as less desirable by-products of the synthesis. In this manner it is possible, according to the relative proportions of the dilute gas mixture, not only to facilitate the performance of the synthesis under pressure, but also to control the reaction to a certain extent. The addition of benzine vapours to the dilute recycle gas increases the working life of the catalyst because an automatic extraction of the high-boiling substances which impair the activity of the catalyst takes place to a certain extent.

In a general way, it has been found that the content of admixed gases or vapours desirable in the interests of a smooth reaction may be the greater the higher the pressure employed for the reaction.

In carrying out the invention, the incorporation of the fresh gas can be effected, with particular advantage, approximately midway of the reaction zone, or distributed by stages, over several reaction zones.

The synthesis may be subdivided into several stages, and the separation of the resultant products can be effected during and/or at the end of each stage.

In order to enable the invention to be more readily understood, reference is made to the accompanying drawing which illustrates schematically and by way of example one method of carrying the same into practical effect.

In said drawing, A denotes a Fischer-Tropsch contact furnace of the usual construction, comprising a series of stages, A^1, A^2, A^3, A^4, in each of which the contact-mass is disposed between cooling elements narrowly spaced apart, in the manner usual in the Fischer-Tropsch benzine synthesis.

Dilute synthesis gas enters the contact furnace A at B and, after reaction therein, the reaction products and unconverted synthesis gas issue at C from whence they pass into the usual separating apparatus D from which the liquefiable reaction products are withdrawn at E whilst the unconverted synthesis gas is withdrawn at F. A part of the gas withdrawn at F is recycled back to the inlet B of the contact furnace A, whilst the other part is removed from the cycle at G.

According to the present invention, fresh synthesis gas, relatively rich in carbon monoxide and hydrogen is introduced into the furnace A at one or more of the points H, I, K. By this means a very uniform distribution of the reaction over the whole extent of the contact furnace A is achieved.

Thus, if the whole of the fresh gas were to be introduced into the recycle gas prior to the latter entering the contact furnace A, the main reaction would be concentrated in the zone A^1 and would give rise to danger of overheating in this zone and to the increased formation of undesirable by-products.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the catalytic conversion of gases containing carbon monoxide and hydrogen, into hydrocarbons containing more than two carbon-atoms in the molecule with the aid of catalysts, as hereinbefore defined, at temperatures between 150 and 265° C., which process comprises supplying to the contact furnace a diluted synthesis gas, applying a superatmospheric pressure in said contact furnace of above 2 atmospheres separating at least a part of the hydrocarbons formed by the said catalytic conversion from the end gas, recycling a part of the end gas to the inlet of the contact furnace, and admitting fresh gas rich in carbon monoxide and hydrogen beyond the point of admission of the recycled end gas, such that the gas undergoing the catalytic conversion always contains more than 20% of inert constituents.

2. The process for the catalytic production of hydrocarbons, substantially as described.

Dated this 2nd day of December, 1937.
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Agents for the Applicants.

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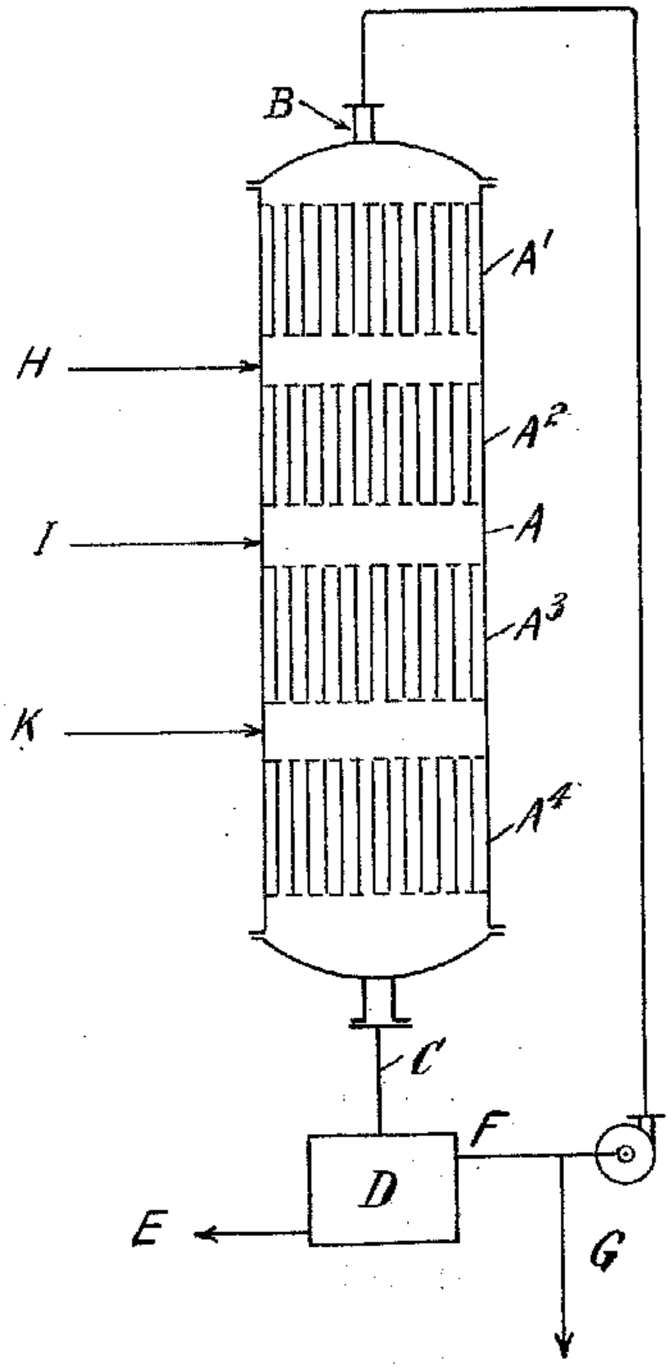
[This Drawing is a full-size reproduction of the Original.]



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