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PATENT SPECIFICATION

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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. 32983/37, 32984/37, 32985/37, and was laid open to inspection on May 31, 1938.)

COMPLETE SPECIFICATION

Improvements in or relating to 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 a process for the production of hydrocarbons by the catalytic conversion of gases containing carbon monoxide and hydrogen with the aid of catalysts.

In the catalytic conversion of gases containing carbon monoxide and hydrogen, at atmospheric pressure and at temperatures below those at which carbon dioxide and methane form the chief products, hydrocarbons of the C_{10} series and downwards, are mainly obtained. In many cases however, a higher yield of solid paraffin is desired, since this product is a valuable originating material for the synthesis of fatty acids.

The catalytic conversion, at atmospheric pressure, of gases containing carbon monoxide and hydrogen was disclosed through the researches of Franz Fischer and his collaborators (" Ges. Abhandlungen zur Kenntnis der Kohle," published by Girardet, Essen (Ruhr), Germany, 1925—1936). Suitable catalysts for this benzine synthesis are the known cobalt- and/or nickel-containing catalysts, the production of which has been described for example by Franz Fischer in the Journal " Brennstoffchemie," Vol. 12, No. 12 (15.6.31), pages 225—244. In the process of the present invention use is preferably made of a catalyst containing 33% of cobalt, 6% of thorium oxide, and 61% of kieselguhr.

It is known that most of the methods leading to an increased yield of paraffin, i.e. working at superatmospheric pressure shorten the working life of the contact mass since the mass gradually becomes clogged with products of high boiling point (" Brennstoffchemie," Vol. 12, pages 365 to 372 and Vol. 14, pages 3 to 8).

The present invention aims at enabling larger yields of paraffin to be obtained than were hitherto possible.

To this end, the process of the present invention comprises, in combination, the steps of disposing the catalysts stationarily in a contact furnace, between cooling elements spaced apart at a distance of the order of 10 mm., and adapted to remove substantially all the heat generated in the reaction, applying a superatmospheric pressure suitably from 2 to 50 atmospheres and more, maintaining a contact period of the gases of more than 1 minute, suitably from 3 to 10 minutes, and withdrawing the paraffin formed during the course of the synthesis from the stationary catalysts to such an extent that the quantity of paraffin present on or in the interior of the catalysts is kept below 100% of the weight of the catalyst (free from paraffin) suitably below 50% and preferably below 30%.

The paraffin formed during the synthesis can be continuously or intermittently removed by means of solvents.

The paraffin content can however also be kept low by other methods than by extraction with solvents. For example, a high vacuum may be periodically established in the contact furnace or the furnace may be steamed-out at regular intervals. Capillary forces may also be employed for removing the paraffin. For example, porous rods or the like (composed, for example, of ceramic material or fritted metal) may be inserted in the interior of the contact mass where they become impregnated with paraffin and conduct the latter downwards so that, for example, it will drip from the rods or the like. It is advantageous to keep the rods, tubes or the like, warmer at the bottom

[*Price* 1/-]

than the top, the dripping of the paraffin being thereby facilitated and a capillary drop established, between top and bottom, which facilitates the diffusion of the paraffin out of the contact mass. The porous bodies may also be heated below to such an extent as to vaporise the paraffin from their surface, this measure again intensifying the capillary flow of liquid paraffin.

In carrying out the invention, further measures for increasing the yield of paraffin may be applied.

Among such measures may be mentioned:—

1. The employment of somewhat thicker catalyst layers, for example of slightly more than 10 mm. (the "thickness" of the contact layers denoting the distance between two cooling elements of the contact furnace).

2. The employment of highly concentrated contact masses, such as those containing more than 40% by weight of hydrogenating metals.

3. The employment of gas mixtures with an excess of carbon monoxide over hydrogen, above the ratio 1:2 especially when using cobalt-containing iron-free catalysts.

4. The employment of gas mixtures containing more than 90% of carbon monoxide plus hydrogen.

The paraffin solvents which may be used in carrying out the invention may be tetralin and other similar solvents, or liquid products of the hydrocarbon synthesis itself may also be used.

Oxygen-containing solvents, such as alcohols, ketones, or stable esters, may also be used.

The effect of the invention is that an accumulation of undesirable substances in the catalyst, which reduce the activity of the latter and the consequent injurious or undesirable effects occur in substantially smaller degree. In this way, again, a uniformly high yield of valuable hydrocarbons is ensured.

The most simple method of carrying out the hereindescribed process is to take catalysts of the hereindescribed type and using superatmospheric pressure pass the reaction gases through the contact furnace from below upwards and (if desired) partially to cool the gases prior to their discharge from the furnace. For example if the exhaust gases be cooled from a reaction temperature of 200° C. down to 100 to 150° C. the higher boiling hydrocarbons alone will be condensed and flow back on to the contact mass rigidly arranged between cooling elements narrowly spaced apart, while vapours of benzine and reaction water will be led away. The reflux oils, on their part, effect the continuous extraction of the paraffin formed in the contact mass, and this paraffin will flow off, in liquid form, below, that is counter to the flow of the gases. By this means the tendency to form paraffin is considerably increased. During the process the temperature of the contact mass is maintained from about 10 to 50° C. higher than would be advisable in the absence of that irrigation, depending on the amount of irrigating liquid used.

In order to keep below 100% loading with paraffin, it is advisable to maintain the amount of irrigating material at least equal to the amount of hydrocarbons produced, the amount being increased on occasion to three to four times the amount, but not ten times the amount.

EXAMPLE I.

1000 kgs. of a contact mass consisting of 33% of cobalt, 6% of thorium oxide (ThO_2) and 61% of kieselguhr as used in the known Fischer-Tropsch synthesis at atmospheric pressure are filled into a contact furnace 3 metres in height, which contains, in known manner, numerous cooling elements, and a 90% synthesis gas, which contains carbon monoxide and hydrogen in the proportion 1:2, is passed through the furnace from above downwards at the rate of 300 N.T.P. cubic metres per hour, calculated upon a gas containing 100% carbon monoxide and hydrogen, a temperature of 190° C. and atmospheric pressure being maintained in the furnace. 120 grammes of liquid and solid hydrocarbons per N.T.P. cubic metre are formed, consisting of 60 grammes of benzine, 50 grammes of oil and 10 grammes of solid paraffin. If the same contact mass is used at a pressure of 12 atmospheres and a temperature of 180° C. and with the same gas throughput (300 N.T.P. cubic metres per hour), 130 grammes of higher hydrocarbons are formed per N.T.P. cubic metre, made up of 30 grammes of benzine, 50 grammes of oil and 50 grammes of solid paraffin. If the same quantity of gas be passed from below upwards through the same contact mass under the same conditions and at a temperature of 185°, the quantity of liquid and solid hydrocarbons formed per N.T.P. cubic metre remains unchanged at 130 grammes, but the proportion of solid paraffin is raised to 65 grammes, the other products being diminished in proportion. If the outgoing gas be now cooled to 125° C. at the top end of the furnace, the higher boiling hydrocarbons will condense, flow back into the furnace and extract the contact mass to an increased extent until the average loading with paraffin amounts to about 50% of the weight of the contact mass. By this extraction the harmful coating of the active zone of the contact material is lessened, so that greater formation of solid paraffin aimed at by the invention occurs. With the same total yield, about 78 grammes of solid paraffin per N.T.P. cubic metre of gas are now produced.

EXAMPLE II.

If the same contact furnace with the same catalyst and the same quantity of gas as in Example I is traversed by the gas from above downwards, and at the same time the catalyst is irrigated at 195° C. with a quantity of 50 kgs. per hour of a preferably unsaturated oil boiling between 150 and 250° C., 70 grammes of paraffin and 60 grammes of oil and benzine, which have to be distilled off from the irrigating oil, are obtained per N.T.P. cubic metre of gas. If the irrigation of the catalyst with the aforesaid oil is increased to 150 kilogrammes per hour with the same quantity of gas (300 N.T.P. cubic metres per hour) and at 200° C. 80 grammes of paraffin and 50 grammes of benzine and oil, i.e. a total of 130 grammes again, are obtained per N.T.P. cubic metre of gas.

In Specification No. 464,308 there has been described and claimed a process for carrying out the conversion of carbon monoxide with hydrogen for the production of liquid, solid and/or gaseous hydrocarbons, in the presence of rigidly arranged catalysts, which comprises trickling media over these catalysts during the conversion while avoiding the formation of a liquid level in the reaction space.

We are also aware that it has been proposed to produce liquid hydrocarbons with the aid of catalysts disposed in a body of liquid and we make no claim to processes of that type.

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 production of hydrocarbons containing mainly paraffin which is solid at room temperature, by the catalytic conversion of gases containing carbon monoxide and hydrogen with the aid of catalysts, said process comprising in combination the steps of disposing the catalysts in a contact furnace between cooling elements narrowly spaced apart and adapted to remove substantially all the heat generated in the reaction, applying a superatmospheric pressure suitably from 2 to 50 atmospheres and more, maintaining a contact period of the gases with the catalysts of more than 1 minute, suitably from 3 to 10 minutes, and withdrawing the paraffin formed during the course of the synthesis from the stationary catalysts to such an extent that the quantity of paraffin present on or in the interior of the catalysts is kept below 100% of the weight of the catalysts (free from paraffin) suitably below 50% and preferably below 30%.

2. Process as claimed in claim 1, in which the paraffin formed is continuously or intermittently removed during the synthesis by means of solvents.

3. Process as claimed in claim 1, in which the paraffin formed is removed during the synthesis by capillary forces (diffusion) for example by means of porous rods, tubes or the like.

4. Process as claimed in any of the preceding claims, in which the reaction gases are led through the contact furnace in the direction from below upwards whereby the reaction products are partially cooled on the upper end of the contact furnace so that the condensing higher boiling hydrocarbons flow back into the contact mass.

5. Process as claimed in any of the preceding claims, in which the thickness of the contact layer, measured from one cooling element of the heat removing unit to another, somewhat exceeds 10 mm.

6. Process as claimed in any of the preceding claims, in which a synthesis gas containing more than one part of carbon monoxide to two parts of hydrogen is employed.

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

8. Hydrocarbons whenever produced by the process claimed in any of the preceding claims.

Dated this 29th day of November, 1937.
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Agents for the Applicants.

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