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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Process for Synthesising Hydrocarbons from Carbon Monoxide and Hydrogen.

We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, a Corporation organised under the Laws of Germany, of 45, Bockenheimer Anlage, Frankfurt-on-the-Main, Germany, and WILHELM HERBERT, a German Citizen, of 45, Haeberlinstrasse, 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 synthesising hydrocarbons from carbon monoxide and hydrogen.

In the catalytic conversion of gaseous mixtures containing carbon monoxide and hydrogen into hydrocarbons which are principally liquids of a paraffinic and olefinic nature, at temperatures below the actual temperatures of methane formation, i.e. below 270 to 300° C. and in particular below 220° C. the process is usually carried out with contact masses consisting of a metal having a hydrogenating action, such as cobalt, nickel, iron, copper, or also mixtures or alloys of these metals, combined with activators consisting of difficultly reducible metal compounds, for example thorium oxide, magnesium oxide, manganese oxide, uranium oxide and the like. As a rule, the contact materials are deposited on carrier substances, such as kieselguhr, silica gel, active carbon. The contact materials are generally produced by precipitating nitrate, chloride or formate solutions of the said metals or mixtures of metals, for example cobalt nitrate plus thorium nitrate, with alkalis, for example an alkali metal carbonate, ammonia or the like, and thereupon—or else during or before the precipitation—uniting the same with the carrier substance.

A highly active contact material is prepared, for example, by boiling up cobalt and thorium nitrate solutions with purified kieselguhr and then precipitating the metals with potassium carbonate, while hot, until the heavy metal ions disappear. The precipitate is subjected to washing with hot water, drying, granulation and reduction with hydrogen at 300° to 400° C. A known advantageous composition comprises 33% of cobalt, 6% of thorium oxide and 61% of kieselguhr. Any of the known catalysts for the synthesis of benzine, oil and solid paraffin at atmospheric pressure by reduction of carbon monoxide are suitable for the process of the present invention (see the publications of Franz Fischer and collaborators in "Brennstoffchemie," Years 1930, 1931, 1932 onwards).

When using such catalysts for the benzine synthesis at atmospheric pressure it has been found convenient to work with gas throughputs of at most 1 N.T.P. litre (i.e. 1 litre when measured at normal temperature and pressure) per gramme of hydrogenating metal (e.g. cobalt) per hour.

In general an ordinary synthesis gas consists of: 28% of carbon monoxide, 56% of hydrogen, 16% of inert substances (nitrogen, carbon dioxide, methane) and the conversion of the CO plus $2H_2$ in the synthesis gas in one or more reaction stages amounts to 50 to 99%.

The bulk density of the catalysts suitable for the benzine synthesis, for example of the aforesaid cobalt catalyst, amounts to about 300 grammes per litre. The quantity of metal, in the example mentioned, amounts to 33% of 300 grammes, i.e. 100 grammes of cobalt per litres of poured contact mass. The throughput of gas for one litre of contact mass (which is accommodated in the usual manner in a thin layer in contact furnaces with numerous cooling elements and utilised at about 180 to 200° C.) amounts thus to 100 N.T.P. litres of synthesis gas per hour.

The time of stay of the gas, referred to the furnace space taken up by the contact material (which is thus equal to the bulk density of the contact material), amounts to one one-hundredth part of an hour, or 36 seconds. (For the purpose of simplifying the calculation, the increase of velocity of the gas owing to the volume of the contact grains and to the rise in temperature of the gas entering the furnace, and also the alteration

[*Price* 1/-]

of the volume of the gas by the contraction resulting from the reaction in the contact furnace, have not been taken into account). Under these indicated conditions, the aforesaid contact mass works with the highest yield and longest life hitherto possible.

For example, the yield of liquid products per N.T.P. cubic metre of the aforesaid synthesis gas amounts to from 100 to 110 grammes (referred to 100% synthesis gas the yields given must be multiplied by the factor 100/84). If the synthesis gas is well precleaned, i.e. freed from hydrogen sulphide, organic sulphur, resin formers and the like—the life of the contact mass is 3 to 4 months. It is assumed here that the synthesis is carried out under approximately atmospheric pressure.

Attempts have already been made to raise the efficiency of the contact materials by increasing the gas throughput about 1 litre per gramme of cobalt (generally speaking, metal having a hydrogenating action), but this resulted in a lower yield and, more particularly, in a shorter life of the contact material; for this reason even smaller gas throughputs than 1 N.T.P. litre per gramme of cobalt per hour are employed as a rule, for example 0.7 N.T.P. litre per gramme of cobalt per hour. Even if elevated pressure is employed in place of the usual normal pressure synthesis, a smaller yield was hitherto obtained when increasing the gas throughput above 1 N.T.P. litre per gramme of hydrogenating metal in the contact mass per hour, as compared with the results when working at the rate of 1 litre per gramme of hydrogenating metal. The circumstances are also not altered by the fact that, when pressure is employed and the temperature is correspondingly lowered, the yields are in general higher than at normal pressure, for example, between 120 and 140 grammes per cubic metre, provided the gas throughput is again 1 N.T.P. litre per gramme of hydrogenating metal per hour.

The present invention aims at increasing the efficiency of the aforesaid synthesis by keeping the heat generated within the contact mass, which is embedded in known manner between closely adjacent cooling surfaces, below a critical limit expressed in kilogramme calories per hour and per square metre of cooling surface.

According to the invention the gas throughput is maintained higher than 1 N.T.P. litre, preferably 2 to 20 N.T.P. litres or more per hour per gramme of hydrogenating metal in the contact mass, and the reaction chamber over which the contact mass is distributed is made of such large dimensions and/or the pressure is maintained so high that the time of stay of the gas in contact with the contact mass becomes greater than 45 seconds, for example 1 to 10 minutes, whilst the reaction temperature is so regulated that the heat evolved by the reaction, calculated as heat load per square metre of cooling surface of the cooling members embedded in the contact mass, at the reaction gas pressure of p atmospheres, does not exceed the value of $500\sqrt[3]{p}$ kilogramme calories per hour.

It is easily possible to ascertain the optimum temperature by first adjusting the gas throughput and time of stay of the gas and then progressively increasing the temperature, for example from 150° C. upwards, but keeping it lower than the temperature at which the heat of reaction to be carried off by one square metre of the cooling elements attains the value of $500\sqrt[3]{p}$ kilogramme calories per hour. It is then maintained at that value at which the optimum yield of the desired liquid hydrocarbons occurs.

As a rule the alteration of the time of stay and gas throughput, in accordance with the present invention, also requires a slight alteration of the temperature, as is apparent from the Examples.

Within the limits of the foregoing figures for the gas throughput and the time of stay, it is advisable, when using superatmospheric pressures, to keep the ratio between the time of stay in minutes and the gas throughput (expressed in N.T.P. litres per gramme of hydrogenating metal per hour) higher than 1:1 and especially at from 3:1 to 10:1.

The process may be carried into practical effect in various ways, which are described in greater detail in the Examples. For example, when working at atmospheric pressure the gas throughput through a contact furnace may be doubled, while using the same amounts of contact material, if the volume of the contact furnace and the surface of the contact furnace carrying off heat are increased to twice or three times their former magnitude, and the contact mass is accordingly spread out by the insertion therein of wire spirals, Raschig rings, and the like. The poured volume of the contact mass is made large, for example by the employment of correspondingly large amounts of carrier masses or correspondingly voluminous carrier masses, for example kieselguhr, active carbon, pumice stone or the like. Both measures, viz. the application of spirals, Raschig rings or the like, or the further dilution of the catalyst by carrier substance may be employed only up to the quintuple enlargement of the initial poured volume of the original catalyst since otherwise the speed of the gases flowing through the contact furnace and/or the dilution of the contact material would be too great to obtain an adequate speed of reaction.

In the case of gas throughputs of more than 2 N.T.P. litres per gramme of hydrogenating metal per hour, and especially when working with superatmospheric pressure it is advisable, in order to ensure controlled withdrawal of heat, no longer to employ the known concentrated contact material, containing, for example, 33% of cobalt metal, suitably spaced out, but to provide for uniform distribution of the metal in the form of a suitably diluted contact material, e.g. by adding more kieselguhr, so that the contact mass contains less than 33% by weight, in particular less than 25% by weight, of hydrogenating metal and that 1 litre of poured contact mass contains less than 100 grammes in particular less than 50 grammes, preferably 10 to 40 grammes of hydrogenating metal.

It is possible to employ contact materials which are highly dilute, for example containing only 2% by weight of cobalt. The low metal contents of the contact mass are particularly useful when low molecular hydrocarbons, from benzine down to gasol (propane and butane, propylene and butylene), are to be produced.

It is particularly advantageous to work with a pressure raised substantially above one atmosphere, for example kept at from 3 to 20 atmospheres. The pressure of 20 atmospheres represents in the first instance the upper limit for contact masses (such as cobalt, nickel and copper-containing contact materials) which facilitate the formation of water in accordance with the equation:

$$CO + 2H_2 = CH_2 + H_2O$$

since in this range of pressures the water of reaction condenses within the contact material at the reaction temperature, and then causes, on the one hand, direct obstructions of the reaction and, on the other hand, increased formation of side-reactions, for example the formation of acids. The pressure range of more than 20 atmospheres may, however, be exceeded if the reaction is carried out only so incompletely in a single passage through the contact material, that the dew point of the water vapour is not reached within the contact chamber. To this end it is possible to work with a plurality of reaction stages or with recycling of the gas, in which case conditions can easily be so regulated that the dew point of water vapour is not reached. Under these circumstances, it is also possible to employ pressures of up to 100 atmospheres, and more, in economical manner, and to attain very high gas throughputs and efficiencies.

For contact masses which facilitate the formation of carbon dioxide in accordance with the equation:

$$2CO + H_2 = CH_2 + CO_2$$

such as iron or iron-copper contact materials, there is no such pressure limit. With such contact materials it is true that products of increasingly higher molecular weight are formed with progressive increase of pressure, unless the increase in pressure is accompanied by an increase in throughput and possibly in temperature; but no pronounced obstruction of the reaction occurs.

When working according to the present invention, high yields, of for example 120 to 140 grammes referred to an 84% synthesis gas, are then obtained despite the use of gas throughputs which are higher than 1 N.T.P. litre per hour and per gramme of hydrogenating metal.

In addition, an unexpected lengthening of the life of the contact materials, and consequently a high permanent yield, are observed when working in accordance with the invention. For example, a contact material containing 12% of cobalt may be used for six months without substantial decline in yield.

A further advantage—particularly of contact masses which contain less than 33% by weight of hydrogenating metals—is the increased formation of benzine, when working in accordance with the invention, together with the suppression of the formation of solid paraffin. To this advantage must be added the more highly olefinic character of the products.

In general, the throughput per gramme of metal of hydrogenating action can be increased the more, the longer the time of stay and the lower the formation of paraffin are kept. For example, it is possible to work with advantage at a pressure of 100 atmospheres, with recycling of gas, with a contact mass containing only 5% of cobalt and an hourly throughput of gas of 10 N.T.P. litres per gramme of cobalt.

A particularly long life of the contact masses is obtained, when working in accordance with the invention, if, besides the gas throughputs indicated, which relate to fresh gas supplied to the contact mass, a part of the gas is recirculated so that the gas velocity is further raised. The formation of paraffin is greatly reduced by recycling when the temperature is suitably selected—and especially when it is increased as compared with optimum working conditions without recycling. The effect is further increased if the recycled quantity of reaction gas from which, if desired, the reaction products have previously been partly or wholly removed, and the temperature are so selected that the hydrogen partial pressure of the gas entering the contact mass, at the pressure p, is smaller than $0.3 \times p^{0.5}$ atmospheres. In this way the deposition of solid paraffin on the active parts of the contact material is diminished and the decomposition products produced catalytically from this paraffin are reduced in quantity, so that the life of the contact material is further unexpectedly lengthened, for example to from 9 to 12 months. This favourable action on the life permits also working with gases which, on entering the contact mass, contain an excess of carbon monoxide over hydrogen beyond the proportion 1:2 in the case of cobalt contact materials, and over the proportion of 2:1 in the case of iron contacts, i.e. in general above the proportion of consumption of CO and H_2 by the catalyst employed. A large proportion of valuable olefinic hydrocarbons are then obtained, which are excellently suited for further chemical treatment, without having to purchase this advantage, as heretofore, at the cost of a shortened life. Without the method of working of the present invention, the life of the contact material is always unsatisfactory when excesses of carbon monoxide beyond the consumption proportion to hydrogen are used.

Of the two main measures of the present invention—namely the increasing of the gas throughput and lengthening of the time of stay, while retaining the heat load calculated per square metre of the cooling elements below the value of $500 \sqrt[3]{p}$ the first (the increasing of the gas throughput) is of advantage also from the standpoint of the plant costs, while the second (lengthening of the time of stay) involves expenditure, which means either expense for the enlarging of the contact furnace, or the incurring of expense for the compression of the gas. To what extent the methods possible in accordance with the invention will combine the two measures (increase of volume and increase of pressure) in detail, is a matter for calculation and consideration of other general questions of operation. If, for example, the cost of power is low and the cost of material high, it is less advisable to obtain the desired time of stay by means of larger contact furnace volumes, than by means of increased pressure, particularly as the yield is thereby generally raised.

Example I.

A cobalt-thorium-kieselguhr catalyst of the composition:

100 parts by weight of cobalt
18 parts by weight of thorium oxide
182 parts by weight of kieselguhr

(corresponding to 33% of cobalt, 6% of thorium oxide and 61% of kieselguhr), the production of which by precipitation from the nitrates and reduction of the carbonates has been described at the outset, is placed in granular form in a contact furnace in layers about 10 mm. in thickness separated by cooling elements preferably cooled by hot water. The contact chamber has a volume of 10 cubic metres available for the contact mass, and the contact filling amounts to three tons. The contact furnace is divided into two stages. Between the two stages a portion of the reaction products is withdrawn. 1000 N.T.P. cubic metres of synthesis gas (consisting, for example, of 28% of carbon monoxide, 56% of hydrogen and 16% of inert substances) are passed per hour through the contact furnace at 180° C. and normal pressure, and a total yield of hydrocarbons of 100 grammes per N.T.P. cubic metre of entry gas, consisting of 15% of solid paraffin, 40% of oil and 45% of benzine, is obtained. The time of stay of the gas in the contact chamber amounts to 10/1000=1/100 hour=36 seconds. The hourly gas throughput amounts to 1 N.T.P. cubic metre per kilogramme of hydrogenating metal (cobalt) in the contact mass. The ratio between the period of stay in minutes and the gas throughput in litres per hour per gramme of cobalt thus amounts to 0.6:1.

The heat load of the cooling surfaces is calculated in the following manner: The contact furnace contains 2000 square metres of cooling surface; of the quantity of $CO+2H_2$ contained in the entry gas= 84/100 of 1000 cubic metres=840 cubic metres, there were still 40 cubic metres in the residual gas, together with the accumulated inert substances and gaseous reaction products, for example methane. Thus, 800 cubic metres were converted, which gave a heat generation of 800×600=480,000 kilogramme calories. Referred to 1 square metre of cooling surface, this makes 240 kilogramme calories per hour.

If the above indicated quantity of contact mass is accommodated in a furnace having a capacity of 20 cubic metres, the volume of the mass being doubled by insertion therein of spacing material, for example wire spirals, Raschig rings, pumice stone and the like, the same amount of contact material (3 tons) permits an hourly gas throughput of 1400 cubic metres, while retaining the yield of 100 grammes per N.T.P. cubic metre (composition 14% of paraffin, 38% of oil and 48% of benzine).

The working temperature, i.e. the temperature of the cooling elements, is preferably kept a few degrees higher in this example, such as 185° C. The time of stay of the gas, referred to the contact furnace space imagined as empty, amounts to 51.5 seconds, and the gas throughput to 1.4 N.T.P. cubic metres per kilogramme of cobalt in the contact mass per hour, the ratio between these two factors thus amounting to 0.86:1.4=0.62:1. The heat load per square metre of cooling surface now amounts to 168 kilogramme calories per hour.

EXAMPLE II.

Instead of spacing out the contact material with the aid of Raschig rings, pumice stone and the like, the process is carried out as in Example I, second part, but with a contact mass to which about twice the amount of kieselguhr was added during its production. For example, a contact mass of the following composition is employed:

100 parts by weight of cobalt
18 parts by weight of thorium oxide
364 parts by weight of kieselguhr
(21% of cobalt, 4% of thorium oxide, 75% of kieselguhr).

The aforesaid contact furnace, having a capacity of 20 cubic metres, is filled with this contact mass, in such a way that the total content of cobalt now once again amounts to 1000 kilogrammes, but now corresponds to 4.8 tons of contact mass. With a gas throughput of 1400 N.T.P. cubic metres, the time of stay once again amounts to 51.5 seconds, and the throughput per gramme of cobalt per hour to 1.4 N.T.P. cubic metres. The yield in this case amounted to 110 grammes of liquid hydrocarbons per N.T.P. cubic metre, consisting of 8% of paraffin, 35% of oil, 57% of benzine.

EXAMPLE III.

The capacity of the furnace was increased to 40 cubic metres and a contact composed of cobalt, thorium oxide and kieselguhr in the proportions: 100:18:728 was employed. At a temperature of 188° C. and a gas throughput of 1400 N.T.P. cubic metres per hour, 115 grammes of liquid products consisting of 6% of paraffin, 30% of oil and 64% of benzine were produced. The time of stay amounts in this case to 103 seconds, and the gas throughput to 1.4 N.T.P. cubic metres per gramme of cobalt per hour. The ratio between the time of stay and the gas throughput amounts to 1.72:1.4=1.23:1.

EXAMPLE IV.

As the enlarging of the furnace capacity beyond a certain degree becomes uneconomical, the enlargement of the furnace space is replaced, or accompanied by an increase in the working pressure, whereby the time of stay can be increased to a multiple.

For example, the operation is carried out with a contact material consisting of 100 parts of cobalt, 18 parts of thorium oxide and 364 parts of kieselguhr, a contact furnace having a capacity of 15 cubic metres, at a working pressure of 12 atmospheres, a working temperature of 195° C., and a gas throughput of 1500 N.T.P. cubic metres per hour. With 750 kilogrammes of cobalt in the contact chamber, the gas throughput amounts to 2.0 litres per gramme of cobalt per hour, and the time of stay to 7.2 minutes. The yield then amounts to 130 grammes of liquid products per N.T.P. cubic metre and consists of 20% of paraffin, 35% of oil, and 45% of benzine. The ratio between the time of stay and the gas throughput amounts to 7.2:2=3.6:1.

EXAMPLE V.

If the end gases produced by operating as in Example IV are recycled back to the contact chamber, in an amount equal to twice that of the fresh gas, the same yield is obtained at 200° C., but there is a lengthening of the life of the contact material from 4 to 9 months. In addition, considerably more benzine (64%) and less paraffin (6%) are produced with the yield indicated.

In the case of gas throughputs over three litres per gramme of cobalt per hour, for example 5 to 10 litres, and times of stay of the gas in the contact chamber below 8 minutes, the paraffin formation can be practically completely eliminated.

With an excess of carbon monoxide in the gas entering the contact mass, beyond the proportion of the consumption of carbon monoxide and hydrogen, valuable highly olefinic benzines and oils are obtained, particularly when the gases are recycled.

EXAMPLE VI.

240 kgs. of a contact mass, containing 12 kgs. of cobalt, 2 kgs. of thorium oxide and 226 kgs. of Kieselguhr, are charged in a contact chamber having a capacity of 1 cubic metre, with distances of 20 mm. between the cooling surfaces, at 220° C. and 100 atmospheres pressure, with 120 N.T.P. cubic metres of synthesis gas per hour. The reaction end gas is admixed with the fresh gas, after cooling in a heat

exchanger and separation of the products then condensing. The amount of recycle gas amounts to 600 N.T.P. cubic metres per hour (at 100 atmospheres pressure).

A yield of 145 grammes of liquid products—consisting predominantly of oil and benzine—is obtained per N.T.P. cubic metre, corresponding to a yield of 178 grammes per N.T.P. cubic metre of originating gas excluding inert gases.

The gas throughput amounts in this example to 10 N.T.P. litres per gramme of cobalt per hour. The time of stay amounts to 50 minutes, as the recycled quantity is not taken into account. The ratio between the time of stay and the gas throughput amounts to 5:1. The heat load is obtained as follows: Out of 120 N.T.P. cubic metres of entering gas, 98 cubic metres of $CO+2H_2$ are converted, which generate a quantity of heat of $98\times600=58800$ kilogramme calories. With a cooling surface in the contact furnace of 100 square metres, the heat load thus amounts to 588 kilogramme calories per square metre per hour.

EXAMPLE VII.

The gas throughput in Example VI is trebled, and the recycle quantity quintupled. At 240° C. a yield of 140 grammes of benzine and gasol hydrocarbons per N.T.P. cubic metre of originating gas is obtained. The heat load of the cooling surfaces now amounts to 1750 kilogramme calories per square metre per hour, i.e. still less than the upper limit of the invention, of $500\sqrt[3]{p}=2320$ kilogramme calories per square metre per hour.

EXAMPLE VIII.

The gas throughput in Example VII is further doubled, and the furnace temperature is increased to 255° C. in order to retain the same relative gas conversion as in Example VII. Only 70 grammes of benzine and gasol are produced, the remaining products being predominantly methane and carbon dioxide. The heat load of the cooling surfaces amounts to 3600 kilogramme calories per square metre per hour.

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 gaseous mixtures containing carbon monoxide and hydrogen, into hydrocarbons which are principally liquid or solid at normal temperature and mainly of paraffinic and olefinic nature, with catalysts known for the synthesis at atmospheric pressure of benzine, oil and solid paraffin (Fischer-Tropsch benzine synthesis) and at temperatures lying below the temperature required for the exclusive formation of methane, characterised in that the gas throughput is kept greater than 1 N.T.P. litre, preferably 2 to 20 N.T.P. litres or more per hour per gramme of hydrogenating metal in the contact mass, and that the reaction chamber over which the contact mass is distributed and/or the pressure is or are made so great that the time of stay of the gas in contact with the contact mass becomes greater than 45 seconds, for example 1 to 10 minutes, whilst the reaction temperature is so regulated that the heat generated by the reaction, calculated as heat load per square metre of cooling surface of the cooling members embedded in the contact mass, at the reaction gas pressure of p atmospheres, does not exceed the value of $500\sqrt[3]{p}$ kilogramme calories per hour.

2). Process as claimed in claim 1, in which the space required by the contact mass is increased by disposing the contact grains in spaced out fashion, so as to increase the distance between the contact grains by the insertion therein of spacing material such as Raschig rings or wire spirals.

3). Process as claimed in claim 1 or 2, in which for the purpose of maintaining the time of stay, the bulk density of the contact mass is made large, for example by the employment of suitably large amounts of carrier masses or suitably voluminous carrier masses, for example kieselguhr, active carbon, pumice stone or the like.

4). Process as claimed in claim 3, in which contact masses containing less than 33% by weight, in particular less than 25% by weight, of hydrogenating metal with so voluminous a carrier mass are employed, that less than 100 grammes, in particular less than 60 grammes, preferably 10 to 40 grammes of hydrogenating metal are contained in one litre of contact mass.

5). Process as claimed in any of claims 1 to 4, in which when using pressures of more than 20 atmospheres and catalysts chiefly forming water in addition to hydrocarbons, the reaction is carried out to such an incomplete extent, during a single passage of the synthesis gas through the contact material that the dew point of water vapour is not reached within the contact chamber.

6). Process as claimed in any of the preceding claims, in which, when using superatmospheric pressures, the ratio between the time of stay of the synthesis gases in contact with the contact mass, expressed in minutes, and the gas throughput, expressed in N.T.P. litres per gramme of metal of hydrogenating action per hour, is greater than 1:1, for example from 3:1 to 10:1.

7). Process as claimed in any of the preceding claims, in which the synthesis is performed in a plurality of contact chambers connected in series.

8). Process as claimed in any of the preceding claims, in which the end gases of the reaction are recycled and admixed with the synthesis gas, and the reaction products are if desired, partly or wholly previously removed from the end gas.

9). Process as claimed in any of the preceding claims, in which the proportion between carbon monoxide and hydrogen in the synthesis gas is higher than 1:2 in the case of cobalt catalysts, and in particular greater than the proportion of consumption by the contact mass employed.

10). Process as claimed in any of the preceding claims in which the volume of the contact furnace is increased up to the quintuple of the loose volume of the contact material.

11). The process for synthesising hydrocarbons, substantially as described.

Dated this 25th day of April, 1938.

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