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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the Catalytic Synthesis of Hydrocarbons

(A communication to me from abroad by METALLGESELLSCHAFT AKTIENGESELLSCHAFT, of 45, Bockenheimer Anlage, Frankfurt-on-the-Main, Germany, a Corporation organised under the Laws of Germany.)

I, WILLIAM HANS ARNOLD THIEMANN, Chartered Patent Agent, of 14 to 18, Holborn, London, E.C.1, a British Subject, 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 catalytic conversion in the gaseous phase, of gases containing carbon monoxide and hydrogen, into hydrocarbons containing more than two carbon atoms in the molecule and mainly of olefinic and paraffinic nature, at elevated temperatures below those at which methane would normally be exclusively formed, i.e. at temperatures lying between 150° and 300° C. and under a pressure above 2 atmospheres and especially under pressures of between 10 and 100 atmospheres absolute.

Various processes and catalysts have been proposed for the conversion of gas mixtures containing carbon monoxide and hydrogen at elevated temperature and under superatmospheric pressure, into gaseous, liquid and solid hydrocarbons. Previously proposed catalysts for this purpose consist for example of hydrogenating metals such as iron, nickel or cobalt, activators such as oxides of the rare earth metals, or of aluminium, zinc or the alkali metals and on occasion a carrier such as pumice stone. Moreover in the previously proposed processes it has been suggested to employ mixtures of carbon monoxide and hydrogen containing a proportion of inert constituents such as carbon dioxide and nitrogen.

The present invention is concerned with highly active catalysts of the type known to be suitable for the Fischer-Tropsch benzine synthesis at atmospheric pressure and at temperatures below those at which methane would be the chief reaction product (i.e. at temperatures lying between 150 and 265° C.) and capable under those conditions, of producing more than 100 grammes of liquid and solid hydrocarbons per N.T.P. cubic metre of synthesis gas calculated on the basis of a gas containing only carbon monoxide and hydrogen.

Such catalysts consist of a hydrogenating metal (especially cobalt), an activator and more than 50% of kieselguhr, which latter serves as carrier substance, and they have been described for example in "Brennstoffchemie" 1932, Vol. 4, page 61 et seq.

When used in syntheses carried out under superatmospheric pressure, catalysts of the foregoing type have been found to give unsatisfactory results or even to be useless, on account of their activity being too high, which results in the pores of the catalyst becoming choked with paraffin and other reaction products.

The present invention aims at obviating the drawbacks arising when the hereinbefore defined catalysts are employed for syntheses carried out under superatmospheric pressure.

To this end, the present invention provides a process for the catalytic conversion in the gaseous phase, of gases containing carbon monoxide and hydrogen, into hydrocarbons containing more than two carbon atoms in the molecule (and mainly of olefinic and paraffinic nature) at temperatures lying between 150° and 300° C. and under a pressure above 2 atmospheres (especially under pressures of between 10 and 100 atmospheres absolute), characterised by the use of catalytic material as hereinbefore defined, of the type containing hydrogenating metal (especially cobalt) an activator (especially thorium oxide) and more than 50% of kieselguhr and by the application of one or more or all of the following measures viz:—

a) The use of catalytic material containing between 0.5 and 50 grammes of hydrogenating metal per litre of its poured volume;

b) The use of catalytic material having an activator content below 18% calculated on hydrogenating metal;

c) The use of used catalytic material of impaired activity;

d) Dilution of the synthesis gases especially by the admixture to the synthesis gas of recycle gases or of gaseous reaction products of the synthesis.

The invention may be carried out by using a diluted synthesis gas containing more than 20% of inert constituents and/or diluted metallic catalysts containing less than 33% of hydrogenating metal and especially less than 50 grammes, e.g. 40 grammes but not less than 0.5 gramme of hydrogenating metal per litre of contact mass, and/or by using catalysts having a low activator content below 18%, calculated on the quantity of activated metal.

According to one embodiment of the invention, the composition of the herein defined catalysts is modified in such a manner that their activity as regards the formation of hydrocarbons appears lessened, when they are used under atmospheric pressure.

According to another embodiment of the invention the synthesis gas—which as a rule contains up to 30% of carbon monoxide and up to 60% of hydrogen—is diluted by increasing the inert gas constituents to above 20%. The synthesis gas can be diluted in the most diverse ways, for example by using for the synthesis under elevated pressure, an end gas produced in the known benzine synthesis under atmospheric pressure by the Fischer-Tropsch method, or by using the end gas produced in the methanol synthesis, or by merely constantly recycling a part of the end gas produced in accordance with the process of the present invention into the current of fresh originating gas.

The admixture of the fresh gas to the recycle gas need not necessarily be effected before entry into the contact furnace; it is, in fact, possible with particular advantage, to effect the admixture of the fresh gas about in the middle of the reaction zone, or distributed stagewise in equal or unequal portions over a plurality of reaction zones beyond the place where the regenerated gas enters the synthesis furnace. A more uniform distribution of the reaction over the whole contact furnace is thereby achieved, while otherwise the main reaction is concentrated on the zone of entry of the gas, when, in turn, the danger of overheating and the increased formation of undesirable by-products occurs.

A diluted synthesis gas may be produced in a most simple manner by first starting in known manner with a normal technical synthesis gas containing about 12% of inert gas constituents, and causing the same to react under atmospheric pressure with the known catalysts of the Fischer-Tropsch benzine synthesis, as described, for example, in the periodical "Brennstoffchemie" 1932, Vol. 4, page 61 onwards. The resulting end gas, after separation of a portion or all of the reaction products formed, is now compressed to such a degree, if necessary that the partial pressure of the reacting gas constituents (carbon monoxide and hydrogen) is approximately equal to or exceeds the partial pressure of the same gas constituents contained in the initial gas of the previous Fischer-Tropsch synthesis. In the thus diluted form in respect of its content of carbon monoxide and hydrogen said compressed gas is then converted in a second contact furnace, if desired in a plurality of stages, under elevated pressure with the same catalysts (for example 33% of Co, 6% of ThO_2 and 61% of kieselguhr).

The reaction temperatures in the stage or the stages of the pressure part of the catalysis may be made equal to those that are customary for the synthesis under atmospheric pressure. But lower or higher temperatures may also be employed. This depends, for example, on the condition of the contact mass, the pressure level and the velocity of the gas, which according to the invention may be higher than 1 NTP litre per gramme of cobalt in the contact mass and per hour preferably above 1.6 NTP litres (see Example).

In general, lower temperatures will be used with a fresh contact mass at a higher pressure and at low velocities, while with a lower pressure or higher velocities of the gas or old contact mass a higher reaction temperature is preferable.

EXAMPLE.

A synthesis gas of the composition: 4% of N_2, 2% of CO_2, 4% of CH_4, 30% of CO and 60% of H_2 (so-called fresh gas) is passed over a catalyst consisting of 33% of Co, 6% of ThO_2 and 61% kieselguhr rigidly arranged in a furnace between narrow cooling elements known in the Fischer-Tropsch benzine synthesis at a temperature of 185° C. and at atmospheric pressure with a velocity of one NTP litre of carbon monoxide and hydrogen per gramme of cobalt per hour, and a yield of 110 grammes of benzine, oil and paraffin is obtained. If this normal synthesis gas is diluted with the end gases resulting from this pressureless synthesis by recycling methods, the quantity of recycling gas being for example three times the quantity of fresh gas at the same temperature and pressure, a diluted synthesis gas is obtained, composed approximately of 10% of N_2, 6% of CO_2, 17% of CH_4 + homologues, 22% of CO and 45% of H_2. If once again the fresh gas throughput is kept at 1 NPT litre carbon monoxide and hydrogen per gramme of cobalt per hour, referred to 100% $CO+H_2$ in the fresh gas, only 95 grammes of liquid and solid hydrocarbons per NTP cubic metre of fresh gas calculated on 100% $CO+H_2$ are obtained at atmospheric pressure and a temperature of 190° C.

When now a pressure of 12 atmospheres and a temperature of 180° C. are used under otherwise identical conditions, especially as regards the fresh gas throughput expressed in NTP litres per hour, 121 grammes of liquid and solid hydrocarbons, and at 60 atmospheres and 174° C. as much as 138 grammes of liquid and solid hydrocarbons per NTP cubic metre of fresh gas are obtained. If, finally, the pressure is increased to 200 atmospheres, it is advisable still further to increase the dilution of the gas on entry into the contact furnace, for example by more intensive recycling of the end gas, so that the gas entering the contact furnace has approximately the following composition:—

20% of N_2, 13% of CO_2, 42% of CH_4,
8% of CO, and 17% of H_2

With this diluted synthesis gas, at a temperature of 170° C. and at 200 atmospheres pressure and under the same conditions as regards the catalyst, 148 grammes of liquid and solid hydrocarbons are then obtained per NTP cubic metre of fresh gas (calculated for a 100% $CO+H_2$ containing gas).

In order profitably to utilise the end gas resulting from the above described catalytic conversions carried out under superatmospheric pressure, which still contains carbon monoxide and hydrogen, said end gas is preferably again subjected to the same catalytic conversion under superatmospheric pressure in a second contact furnace.

The end gas from the hereinbefore described synthesis carried out at 12 atmospheres pressure, may for instance contain on an average about 10% of carbon monoxide and 20% of hydrogen, after it has passed through one or more contact furnaces with multiple recycling. If this end gas, which represents a 30% synthesis gas, is passed into a further contact furnace working without recycling, 30 to 40 grammes of higher hydrocarbons may still be produced per cubic metre of end gas. If recycling were also employed in this further furnace, only 20 grammes of liquid hydrocarbons would still be produced at the best, quite apart from the more expensive method of operation of recycling.

In view of the low synthesis gas content of the end gas of the first stage, the further stage in the absence of recycling, will preferably be operated with longer treatment times, higher temperature, higher contact activity (for example more concentrated contact material) or also with further elevated pressure; each of these measures can be used alone or all together.

The ratio of carbon monoxide to hydrogen in the gases fed to the first furnace group working with recycling can be kept at 1:2. However, a gas more rich in carbon monoxide may also advantageously be selected, thus obtaining better antiknock products and at the same time a longer life of the contact. The outgoing gases of the first contact furnace group then naturally likewise contain a gas richer in carbon monoxide. As this gas is too poor in hydrogen for further conversion, it will preferably be corrected, for example, by the admixture of hydrogen or by converting a part of the CO content into H_2 with the aid of steam before passing into the second contact furnace group working without recycling.

Instead of the arrangement in series of separate contact furnace systems, the recycling may also be restricted to one part of the furnace length in a single contact furnace, while only the second part of the furnace is operated without recycling.

The two measures for the modification of the composition of the catalyst and the gas composition of the gas prepared for the synthesis may be combined together and with the conditions of temperature and pressure in manifold ways, particularly when the catalysis is carried out in a plurality of stages, which may at the same time be stages of different pressure.

Examples of individual catalysts, temperatures and pressures to be employed for the pressure synthesis of the invention, and also the connection of the various contact stages, are described in greater detail below.

The catalysts with which the present invention is concerned, consist of a metal or mixture of metals having a hydrogenating action, for example cobalt or nickel. In addition, they contain metallic compounds (for example of an oxidic nature, such as oxides, carbonates or the like), which can be reduced only with difficulty or not at all, by hydrogen. These metallic compounds raise the yield considerably above the degree that may be attained by the metal of the catalyst alone. They are herein referred to as activators. This actual catalyst (metal or mixture of metals plus activators) is deposited in a finely divided form on to kieselguhr so that the resulting product consists to an extent of more than 50% of kieselguhr.

It is known that the percentage of activators, referred to the metallic portion of the catalyst, must be kept within definite, fairly narrow limits with a view to obtaining high yields; cf. "Brennstoffchemie", Vol. 12, Page 225, 1931. In that publication the optimum content of thorium oxide in a cobalt-thoria catalyst, is given as 18% of ThO_2 referred to the cobalt content. With either a lower or a higher content of activator the yield and also the life of the contact fall off considerably when carrying out the synthesis at atmospheric pressure.

It has now been ascertained that the synthesis under elevated pressure, for example 2 to 20 atmospheres pressure and over, which heretofore has not been successful with the hereinbefore defined highly active catalysts, may be carried out with complete success if the percentage of activated metals and/or activators in the catalyst is substantially reduced beneath the optimum content for conditions of atmospheric pressure.

For example, in the synthetic production of hydrocarbons from carbon monoxide and hydrogen at a pressure of 10 atmospheres, a catalyst was used which contained only 12% of thorium oxide or, if desired, only 5% of thorium oxide, referred to the metallic cobalt present. With this catalyst a yield of 130 grammes of liquid products was obtained per NTP cubic metre of synthesis gas calculated on a 100% $CO + H_2$ containing gas without recycling. At the same time it was found to be convenient greatly to reduce the proportion of catalyst relatively to the kieselguhr carrier material. For example, the aforesaid cobalt-thorium oxide-kieselguhr catalyst, according to the invention, contained only 25 grammes of cobalt per litre of poured volume of the loose contact material whereas a normal contact for a synthesis carried out at atmospheric pressure with 33% cobalt, 18% of thorium oxide (based on the amount of cobalt) and 61% of kieselguhr, contains 100 grammes of cobalt per litre of the loose contact mass.

The ratio of the catalyst to the kieselguhr carrier can be varied with the pressure of the synthesis. For example, when a pressure of 3 atmospheres is to be used, a catalyst with a metal content of from 20 to 50 grammes per litre of loose poured volume may be employed. For pressures of, for example, 10 atmospheres a catalyst containing from 5 to 25 grammes of active metallic substance per litre of loose volume is suitable. When working with a pressure of 100 atmospheres, these figures are changed to from 0.5 to 10 grammes.

The thorium oxide may be replaced by other activators, for example oxides or carbonates of uranium, aluminium, magnesium, manganese, zirconium, beryllium, cerium, titanium, chromium or zinc, and the ratio of such activators to the hydrogenating metal can be varied in the manner hereinbefore set forth. The rule generally applies that the content of such activators and/or hydrogenating metals must decrease as the pressure used for the synthesis rises.

A catalyst suitable for the pressure synthesis may also be obtained by incompletely reducing the metal acting as a hydrogen acceptor in the production of the catalyst. For example, cobalt hydroxide or cobalt carbonate precipitated on kieselguhr may be reduced with hydrogen in such a way that only 90 to 95% or even 40 to 70% of the cobalt is converted into the metallic form.

In many cases it is advisable to form the contact material out of a plurality of layers, in each of which the catalyst possesses different activator and/or metal contents; for example, the smallest content of activator and/or activated metal is chosen at the point of entry of the gas and the greatest at the point of exit of the gas.

The yield and the life of the contact materials may further be increased by maintaining at the point of entry of the gas a lower temperature than in the other parts of the contact material or a part thereof; for example, the temperature may be allowed to increase from the point of entry of the gas either uniformly or by jerks.

With the foregoing catalysts of lesser activity, when using higher temperatures exceeding 185° C. a higher proportion of benzine (i.e. those hydrocarbon compounds which boil below 200° C. at atmospheric pressure) is obtained.

The same effect is achieved by the use of diluted initial gases.

When older catalysts, which are beginning to lose their activity, are being used, the initial yield may be restored completely or almost completely, when working under pressure, if the throughput of gas is increasingly reduced as the activity of the catalyst falls off. Furthermore, the lessening of the activity of the catalyst may be compensated to a certain extent by increasingly raising the temperature and/or the pressure. When working with diluted initial gas or with recycle gas under pressure it is also possible to counteract the fall in the activity of the contact material by increasing the concentration of the carbon monoxide and/or of the hydrogen, for example by reducing the proportion of recycle gas in the total quantity of entering gas.

The amount of active substance (i.e. hydrogenating metal and/or activator) contained in the catalyst is advantageously adjusted not only to the pressure, under which the synthesis is carried out, but also depending on the composition of the gas to be treated. If the gas contains large amounts of oxides of carbon and hydrogen, highly dilute catalyst is employed, whereas for gases containing small amounts of oxides of carbon and hydrogen, richer catalysts may be used within the scope of the invention and also the catalysts of the known Fischer-Tropsch synthesis with high metal and activator contents.

The process of the invention may also be used when working with a plurality of stages, both when the same pressure is used in all of the stages, and when different pressures are maintained in the different stages. When working with the same pressure in all stages, a somewhat richer catalyst is preferably employed in the succeeding stage than in the first stage. For example, the activity of the catalysts in the various stages is so selected that it increases by stages approximately in the same degree as the amount of oxides of carbon and hydrogen contained in the working gas decreases.

In the same manner, the process of the invention may be carried out when the pressure in the succeeding stages is higher than in the first stage, but in this case it is often convenient to employ catalysts of about the same activity in all stages.

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

1). A process for the catalytic conversion in the gaseous phase, of gases containing carbon monoxide and hydrogen, into hydrocarbons containing more than two carbon atoms in the molecule (and mainly of olefinic and paraffinic nature) at temperatures lying between 150° and 300° C. and under a pressure above 3 atmospheres (especially under pressures of between 10 and 100 atmospheres absolute), characterised by the use of catalytic material as hereinbefore defined, of the type containing hydrogenating metal (especially cobalt) an activator (especially thorium oxide) and more than 50% of kieselguhr and by the application of one or more or all of the following measures, viz:—

a) The use of catalytic material containing between 0.5 and 50 grammes of hydrogenating metal per litre of its poured volume;

b) The use of catalytic material having an activator content below 18% calculated on hydrogenating metal;

c) The use of used catalytic material of impaired activity;

d) Dilution of the synthesis gases especially by the admixture to the synthesis gas of recycle gases or of gaseous reaction products of the synthesis.

2). Process as claimed in claim 1, in which the catalytic conversion is effected in several stages in such a manner, that an increase in the inert gas constituents in the gases of reaction is offset by a corresponding increase in pressure in the individual stages.

3). Method of carrying out the process claimed in claim 1, in which the dilute synthesis gas is a final gas which is obtained in the hydrocarbon synthesis at atmospheric pressure or at a substantially atmospheric pressure (Fischer-Tropsch benzine synthesis) and which is best obtained after separating a part or all of the products of reaction, the final gas being compressed to such a degree, if necessary, that the partial pressure of the reacting gas constituents (carbon monoxide and hydrogen) is approximately equal to or exceeds the partial pressure of the same gas constituents contained in the initial gas of the previous Fischer-Tropsch synthesis.

4). Process as claimed in claim 3, in which the dilution of the initial gas of the hydrocarbon synthesis takes place under pressure by constantly recycling into the initial gas a part of the final gas obtained after separating a part of the products of reaction formed in same, the quantity of recycled gas being a multiple of the quantity of fresh gas, if desired.

5). Process as claimed in claim 1 or 4, in which one or several synthesis furnaces, working with recirculation of the final gases into the reaction gas, is or are followed by one or several synthesis furnaces working without recirculation of the final gases.

6). Process as claimed in claim 5, in which the synthesis furnaces operating with recirculation are operated with a gas mixture containing more than one volume of carbon monoxide per two volumes of hydrogen and in which the composition of the final gases before or on entering the synthesis furnaces operating without recirculation is corrected with regard to its hydrogen content.

7). Process as claimed in any of the preceding claims, in which the diminution in the activity of the catalyst during its working life is counteracted by reducing the gas throughput or, when using recycle gas, reducing the ratio of recycle gas to the total quantity of entering gas.

8). Process as claimed in any of the preceding claims, in which the catalyst employed is one which has been obtained by incompletely reducing the metal acting as hydrogen acceptor.

9). The process for the catalytic synthesis of hydrocarbons, substantially as described.

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

Dated this 2nd day of December 1937.
ALBERT L. MOND & THIEMANN,
14 to 18, Holborn, London, E.C.1,
Agents for the Applicant.

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