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PATENT SPECIFICATION

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3664

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Nov. 25, 1937:

Corresponding Applications in United Kingdom

No. 22734/38
No. 22735/38 } *dated July 30, 1938.*

(One Complete Specification Left under Section 91 (2) of the Patents and Designs Acts, 1907 to 1932.)

Specification Accepted: March 4, 1940.

COMPLETE SPECIFICATION

Synthesis of Hydrocarbons which are Solid, Liquid or readily Liquefiable from Carbon Monoxide and Hydrogen

We, STUDIEN- UND VERWERTUNGSGESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG, of 2, Kaiser-Wilhelm-Platz, Mülheim-Ruhr, Germany, a Body Corporate organised and existing under the Laws of the German State, 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:—

It is known that oxygen-containing compounds, for example methanol and such as are known under the name Synthol, can be produced from carbon monoxide and hydrogen by the use of high pressures and of temperatures of 400° C. or over. It is further known that experiments have been carried out in which products consisting partly of oxygen-containing compounds and partly of hydrocarbons have been obtained using iron contact masses or catalysts that are produced by the decomposition of ferric nitrate, under a pressure of from 10 to 15 atmospheres. Finally, it is known that hydrocarbons are obtained from carbon monoxide and hydrogen at ordinary pressure with iron contact masses or catalysts. According to the literature on the subject, it is possible to obtain with iron contact masses or catalysts at atmospheric pressure, yields of aliphatic hydrocarbons of about from 30 to 35 gm. per cubic metre of a mixture of carbon monoxide and hydrogen, that is to say during a period of as long as about 8 days, while after this time the catalysts function with still less efficiency. The yields that were obtained with precipitation contact masses or catalysts and with decomposition contact masses or catalysts were approximately the same ("Brennstoffchemie", Volume 16, page 2. 1935).

Among other proposals which have been made for reacting together carbon monoxide and hydrogen with the aid of iron catalysts may be mentioned one designed for the production of gaseous olefines together with saturated gaseous hydrocarbons which consisted in passing a gas mixture containing an oxide of carbon and hydrogen, preferably under elevated pressure, at elevated temperatures over a catalyst comprising at least one of the metals iron and cobalt at a substantially lower velocity than that required for the production of mainly liquid hydrocarbons or derivatives thereof. One method of preparing the catalyst in this proposal consists in reducing a joint precipitate obtained from iron and palladium chlorides or nitrates with hydrogen. The gas passed over such catalyst contained more hydrogen than carbon monoxide although in other examples of this proposal the gas passed over an iron-containing catalyst not produced by reduction contained more carbon monoxide than hydrogen.

It has now been found that hydrocarbons that are solid, liquid or readily liquefiable can be produced in an advantageous manner from gases containing carbon monoxide and hydrogen in equal amounts or containing more carbon monoxide than hydrogen under pressures between 2 and 10 atmospheres and at temperatures below 320° Centigrade in the presence of iron catalysts, if the catalysts are conditioned by a preliminary treatment with gases containing carbon monoxide under normal pressure or under some other pressure that is lower than the pressure used in the subsequent production of hydrocarbons.

If the preliminary treatment is carried out under atmospheric pressure, at a temperature of for example 250° Centigrade, this preliminary treatment takes about 5 hours. If, after this preliminary treatment, the pressure is changed to for example 15 atmospheres, a high production of the desired hydrocarbons is directly obtained. If working is, however, commenced without preliminary treatment directly at a pressure of 15 atmospheres, the same high production cannot be attained.

According to the invention, astonishingly good yields of liquid hydrocarbons, the majority of which have a low boiling point, can be obtained over long working periods. In industrial operation it is advantageous to use mixtures of carbon monoxide and hydrogen which contain the carbon monoxide in an amount which is at least the amount required by the equation

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

that is to say at best from $2CO : 1H_2$ up to $1CO : 1H_2$. Whereas complete conversion of such a gas mixture was not possible at ordinary pressure or when starting operation under synthesis pressure it has been found that this conversion can be carried out practically quantitatively at a raised pressure between 2 and 100 atmospheres after the catalyst has been first subjected to a preliminary treatment according to the present invention, for example at atmospheric pressure.

Advantageously the pressure and temperature are determined in the synthesis in relation to each other. This is shown in the accompanying drawing. Along the abscissa are given the working temperatures and along the ordinate the pressures. The straight line *a* indicates for various working pressures the lower temperature limit, at which the hydrocarbon synthesis can be carried out with a sufficiently high conversion. The straight line *a* shows that the working temperature to be employed at the commencement of the operation must be selected to be higher according as the pressure selected rises. The straight line *b* shows the upper temperature limit at which it is possible to work while forming liquid hydrocarbons. It is about 310° C. at pressures from 10 to 90 atmospheres. At higher temperatures other reactions involving the formation of gaseous and oxygen-containing products start gradually to predominate. The inside shaded area of the drawing indicates the physical conditions under which the optimum results are secured when employing iron catalysts and synthesis gas rich in carbon monoxide. If for example the pressure be 10 atmospheres a partial conversion in the direction desired is secured at Point 1 (temperature 230 to 235°). If the temperature be raised to Point 2 (in this case approximately 240°), maximum yields of liquid hydrocarbons are secured, that is 100 to 150 gm. per cubic metre of synthesis gas according to the volume of gas passed through. The greater part of the final gas then consists of carbon dioxide, inert constituents that may be present, gasol that is also formed and gaseous hydrocarbons. There is furthermore produced solid paraffin and a few grammes of water per cubic metre of gas. If it is desired to continue operation during long working periods, it is advantageous gradually to increase the working temperature by, for example, about 2 to 3° per week in order to maintain the conversion constant. From Point 2 to Point 3 there are available almost 60°. If an optimum conversion (that is to say a substantially complete conversion) of the carbon monoxide is not required, the temperature may be raised for a further short period up to about from 305 to 310°. At 30 atmospheres the lower optimum temperature limit in the use of the hereinbefore described contact mass or catalyst and gas mixture is at from 250 to 255° (Point 6 on the drawing). Up to Point 7 there is available about 47° or approximately five months of working.

The convergence of the lines *a* and *b*, and a^1 and b^1 at the higher working pressures, shows that as the pressure rises the possible working periods become shorter and shorter, since the degree of increase of the working temperature which should advantageously be effected to maintain the conversion constant remains the same under the different pressures.

The drawing shows that pressures above 100 atmospheres cannot be used in the process and that there is a rapid drop in economy at pressures above 50 atmospheres. Finally it will be seen from the drawing that at atmospheric pressure or at a slightly raised pressure it is not possible to secure economic yields. The optimum conditions are between 5 and 50 atmospheres.

Finally, to secure good yields of the higher hydrocarbons it is an advantage to increase the contact period of the gases in the contact chamber to an extent approximately proportional to the working pressure, that is to say to make available at 20 atmospheres pressure a contact period of the gas on the contact mass or catalyst that is twice as great as at 10 atmospheres pressure.

If it is desired to carry off by cooling with water the heat generated during the conversion reactions, it is in certain circumstances advisable to work under a pressure equal to the pressure existing in the water chamber, for example at 260° at 50 atmospheres and so on, because then the contact chambers are not stressed either from the outside or from the inside.

EXAMPLES.

EXAMPLE 1.

Ferrous chloride and cupric chloride (iron: copper=4:1 by weight) are dissolved in water and precipitated while hot with the theoretical quantity of sodium carbonate (instead of sodium carbonate, one may use for example potassium carbonate). The precipitate is filtered off, washed until practically free from alkali. impregnated with 1/8% of potassium carbonate (calculated on iron), dried at 110° C. and granulated or pressed or passed on carriers into the reaction chamber, for example a pressure tube. At first in order to form the catalyst a mixture, for example of carbon monoxide and hydrogen in the proportion of 1:2 by volume, is passed at 240° C. and at atmospheric pressure over the dried precipitate. The contraction of the gas which occurs as the result of its conversion increases over a period of three days slowly to 30%. Pressure is now employed and the process is continued for example under 15 atmospheres and at 260° C with a gas mixture that contains carbon monoxide and hydrogen in the proportion of 3:2 by volume, that is 4 litres of gas (calculated at atmospheric pressure) is passed per hour over each 10 gm. of iron. Contraction increases to 60%. The yields of hydrocarbons amount to from 130 to 150 gm. per cubic metre of gas. 80 to 90 gm. consist of solid and liquid hydrocarbons that run off from the contact mass into a heated vessel that is unaffected by pressure, about 50 gm. per cubic metre consist of highly volatile benzine that is carried away with the waste gas in the form of vapour and can be recovered by means of active carbon or in some other manner, while the remainder consists of the lower hydrocarbons formed, known as gasol. The activity of the contact mass or catalyst remains unaffected for months as the working temperature gradually rises, for example in four weeks by 5° C.

EXAMPLE 2.

A contact mass or catalyst produced from ferric nitrate by thermal decomposition (at temperatures up to about 300° C.) was used, the contact mass or catalyst being first alkalised with 1/4% of potassium carbonate (calculated with respect to iron). This contact mass or catalyst is deposited in suitable contact apparatus in granular or compressed form or on inert carriers. This contact apparatus must ensure the complete removal of the reaction heat and the maintenance of the temperature constant. There is at first a preliminary treatment with a gas containing carbon monoxide such as the synthesis gas itself ($3CO:2H_2$) under atmospheric pressure and at a temperature lying between 240 and 250° C., for 5 to 10 hours. At the end of this period the gas contracts to the extent of about 30% due to conversions of carbon monoxide and hydrogen. A change is now made to a pressure of for example 15 atmospheres and about the same temperature, and about 400 litres per hour of a mixture of carbon monoxide and hydrogen in the proportion of 3:2 by volume is caused to react per kg. of iron present in the contact masses or catalysts. The contraction after conversion rises immediately to about 55%. The final gas contains from about 50 to about 70% of carbon dioxide, while scarcely any water is formed. If the temperature is raised every week by from 2 to 3°, the conversion can be maintained constant for six months. About 110 gm. of liquid hydrocarbons are produced per cubic metre of synthesis gas. Roughly 75% thereof boils at between 30 and 180° C. The content of unsaturated hydrocarbons rises during the working period from about 40 to 70%. The benzine thus secured is a motor fuel free from knock.

In addition to the iron contact masses or catalysts mentioned in the examples others may be used to which have been added substances such as manganese compounds, or diluents such as kieselguhr or silica gel. The use of contact masses or catalysts of iron, instead of nickel and cobalt, is not only an economical advantage but a new technical effect is derived therefrom by reason of the fact that it is now possible by means of the features of the process of the invention to secure, instead of the small yields hitherto obtained with iron contact masses or catalysts that are far inferior to those using cobalt contact masses or catalysts, about the same yields while working for particularly long periods of at least half a year.

The liquid hydrocarbons obtained are distinguished by the fact that about 80% boil at even below 200° C. and by the fact that they have olefine contents of on an average 50 to 60%, whereby the antiknock properties of the fuel are improved as is also their utility for future chemical treatment (for example to produce lubricating oils).

Not only are low boiling liquid hydrocarbons formed but there are also formed considerable quantities of gasol (up to 30 gm. per cubic metre) which by reason of its still higher olefine content is equally suitable for further chemical treatment (to produce polymeric benzine, lubricating oil, alcohols etc.).

We are aware that in specification No. 474,448 there is described and claimed a process for the thermal conversion of carbon monoxide with hydrogen into liquid, solid and/or gaseous hydrocarbons containing more than one carbon atom in the molecule and/or their oxygen-containing derivatives which comprises contacting at a reacting temperature carbon monoxide and hydrogen in the presence of a catalyst which has been prepared by precipitating from a solution of a compound of a metal of the iron group such difficultly-soluble or insoluble compound of the said metal as is easily reducible to the metal by heating in the presence of hydrogen, adding to the precipitated compound such compound of another metal as by heating yields an oxide not reducible to metal by hydrogen below 900° C. and subsequently heating the resulting mixture in the presence of a gas having a reducing action to such a high temperature above 500° C. and for such a long time that a partial sintering of the catalyst takes place.

We make no claim in this specification to any process in which the preliminary treatment of the catalysts with gases containing carbon monoxide is effected by heating such catalysts to such a high temperature above 500° C. and for such a long time that a partial sintering of the catalyst takes place.

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, subject to the foregoing disclaimer, we claim is:—

1. In a process for producing hydrocarbons that are solid, liquid or readily liquefiable, from gases containing carbon monoxide and hydrogen in equal amounts or containing more carbon monoxide than hydrogen under pressures between 2 and 100 atmospheres and at temperatures below 320° Centigrade, in the presence of iron catalysts conditioning the catalysts by a preliminary treatment with gases containing carbon monoxide under normal pressure or under some other pressure that is lower than the pressure used in the subsequent production of hydrocarbons.

2. In the process as claimed in claim 1, using iron catalysts that have been produced from iron salt solutions by precipitation and/or by decomposition of iron compounds and which have been subjected to a preliminary treatment in accordance with claim 1.

3. A process for producing hydrocarbons substantially as hereinbefore described in Examples 1 and 2.

Dated this 29th day of July, 1938.
W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

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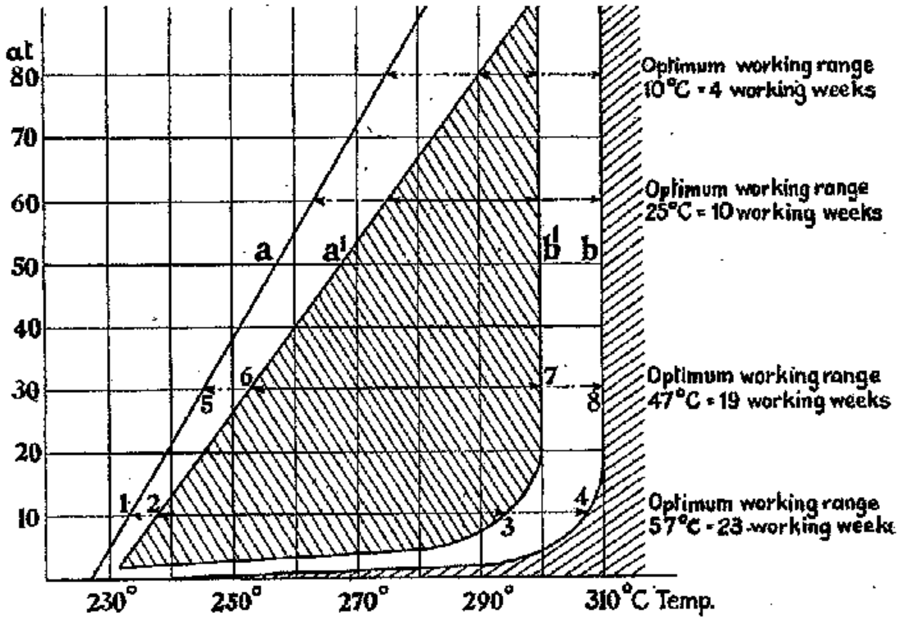
[This Drawing is a reproduction of the Original on a reduced scale.]



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