PATENT SPECIFICATION

709,560

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COMPLETE SPECIFICATION

Process for the Production of Low Boiling Hydrocarbons in the Catalytic Hydrogenation of Carbon Monoxide

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, of 22a, Homberg (Niederrhein), Germany, a German Joint Stock Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the catalytic hydrogenation of carbon monoxide.

In the hydrogenation of carbon monoxide, a mixture of carbon monoxide and hydrogen, conventionally termed "synthesis gas," is brought into contact with a suitable catalyst and is reacted to form aliphatic hydrocarbons of both the saturated and unsaturated type, and also oxygen-containing derivatives thereof. This synthesis has become generically known as the Fischer-Tropsch synthesis, and the general conditions of pressure, temperatures, type and composition of catalyst, and of catalyst, and of catalyst additives essential for such synthesis, are well known and established in the art.

It is also known to effect the synthesis with the catalyst immersed in or coated with a liquid medium, for example, a middle oil, a heavy oil, a paraffin oil, an enthracene oil or a liquid product of the synthesis itself. In such known processes the liquid medium functioned as inert material or as a means of removing the heat of reaction and its molecules did not undergo any diminution in size.

It has now been found that in the synthesis of liquid hydrocarbons boiling up to 200°C. by the catalytic hydrogenation of carbon monoxide carried out in the presence of aliphatic hydrocarbons boiling above 200°C., the synthesis conditions can be so correlated that the said aliphatic hydrocarbons are cracked. The yield of liquid hydrocarbons boiling up to 200°C. and obtained by direct synthesis from the carbon monoxide and hydrogen is thus supplemented by the similar hydro carbons formed as products of the cracking of the aliphatic hydrocarbons boiling above 200°C. Furthermore, when the synthesis conditions are so correlated, hydrocarbons boiling above 200°C. and formed in the synthesis from carbon monoxide and hydrogen are also subject to cracking.

[*Price* 2/8]

According to the invention, a process for the production of liquid hydrocarbons boiling up to 200°C. comprises contacting a synthesis gas containing 0.5-2 volumes of carbon monoxide to one volume of hydrogen with a granular iron catalyst containing an alkali-metal compound (calculated as the alkali-metal monoxide) to the extent of not more than 1% by weight of its total iron content, at a temperature in the range 160°—350°C., at a pressure in the range 2-150 atmospheres and at a space velocity in the range 30-3000 volumes per volume of catalyst per hour in the presence of aliphatic hydrocarbons which boil above 200°C. and which are liquid under the process conditions, the temperature and pressure being so correlated that the said aliphatic hydrocarbons are cracked.

The preferred alkali-metal is potassium and the preferred pressure lies within the range 9-25 atmospheres. The carbon monoxide/hydrogen content of the fresh gas fed to the process should preferably be about 1.5 volumes of carbon monoxide to every volume of hydrogen.

The products of the process according to the invention consist mainly of normally liquid hydrocarbons of a predominantly olefinic character boiling up to 200°C. The conversion to these olefinic materials proceeds with little formation of normally gaseous hydrocarbons, particularly methane and ethane, and the total formation of C_1—C_3 hydrocarbons in relation to the overall yield of marketable synthesis products remains thus at a low order.

The process, in accordance with the invention, may be carried out in any conventional synthesis reactor, and conventional conditions of improved synthesis reaction designed to utilize, or capable of utilizing, a sub-divided catalyst material covered or enveloped by a medium normally liquid at least at the synthesis temperature may be used. The covering or enveloping of the catalyst with the liquid medium may range from a simple coating of the sub-divided catalyst material with the liquid agent to a suspension of catalyst in the liquid medium. Thus, in accordance with the invention, the liquid material for covering or enveloping the sub-divided catalyst may be sprayed from above on to, for example, granular or pelletted catalyst material during the synthesis while the synthesis gas is passed through the catalyst from bottom to top. Alternatively, the sub-divided catalyst material may be completely covered in the reaction zone with the aliphatic hydrocarbons which have boiling points above 200°C. In a further modification, the catalyst may be present as a suspension of relatively finely subdivided particles in the hydrocarbon medium. Any of the conventionally known iron catalyst materials usable for Fischer-Tropsch synthesis may be employed in accordance with the invention, provided they possess an alkali metal content, calculated as the alkali metal monoxide (e.g., K_2O), of not more than 1% by weight of the total iron content. The state of sub-division of such catalyst material and the type of iron catalyst material used should be much and so coordinated that the sub-divided catalyst is comparatively readily wetted by the aliphatic hydrocarbons boiling above 200°C. by which it is to be covered or enveloped. Within the preferred embodiment of the invention, however, the catalyst material is used in the form of dusts or relatively fine grits, permitting the formation of suspensions of the material in the alephatic hydrocarbons boiling 200°C.

Both paraffins and olefins of natural or synthetic origin and free from catalyst poisons are suitable aliphatic hydrocarbons for use in accordance with the process of the invention. These should be liquid at least at the synthesis temperature and pressure, and liquid hydrocarbons of the aliphatic series, boiling above 250°C., or such hydrocarbons which are solid at normal temperatures, and which are, for example, normally produced in major quantities in ordinary catalytic carbon monoxide hydrogenation, are subject to particularly rapid decomposition in the process according to the invention.

Within the preferred embodiment of the invention, the high yields of liquid hydrocarbons boiling up to 200°C. may be still further increased by continuously recycling part of the exit gases, the gases being introduced into the reaction zone together with fresh gas in a ratio of about 1 to 10 volumes of exit gas per volume of fresh gas. Still further increases in yield may be obtained by separating from the recovered low-molecular hydrocarbons and/or from the exit gases hydrocarbon material having a boiling point above 200°C. and reintroducing it into the catalytic reaction zone.

The rate of molecular size diminution of the liquid hydrocarbons boiling above 200°C. greatly depends on operating conditions and catalyst properties, that is to say the decomposition will be the quicker, the lower the molecular size of the synthesis product formed during the hydrogenation of carbon monozide. It has been found, for example, with synthetic paraffin hydrocarbons boiling above 280°C., that the rate of decomposition is 60 grains and more per Ncbm (normal cubic metre) of synthesis gas put through the reactor.

The effect obtained by the process according to the invention depends on the use of a catalyst and of operating conditions which yield a synthesis product rich in liquid hydrocarbons boiling below 200°C., whilst the operating conditions are so correlated that cracking of the aliphatic hydrocarbons boiling above 200°C. is effected. The residence time of the said aliphatic hydrocarbons in the synthesis zone must be sufficient to permit the cracking to proceed. The decomposition of the said aliphatic hydrocarbons into predominantly low molecular olefines in the process according to the invention, is not explained by the recently published assertion that the curve of molecular size distribution of the decomposition products of hydrocarbons is similar to the corresponding curve for a synthesis product (see H. Koch & W. Gilfert, Brennstoff-Chemie, 30, 213, 1949). Contrary to what might have been expected from this assertion, the decomposition product obtained by the process of the invention, though having the same high olefine content as the synthesis product, does not show any additional formation of methane by reason of the decomposition. This is a noteworthy point of basic difference between molecular size diminution as provided in the invention and that of all other known cracking processes.

With the iron catalysts used, the alkali metal content, expressed in terms of alkali metal monoxide, should not exceed a margin to be governed by catalyst concentration and synthesis temperature. When using suspended iron catalysts in the process of the invention, the iron content may be as much as 20-500 grams of iron per litre of catalyst suspension liquid, while the alkali metal content (expressed as the monoxide) should preferably range between 0.15 and 2 grams per litre of the catalyst suspension liquid.

EXAMPLE 1.

A pressure-resistant reactor, 3 metres in height, was charged from below through a finely perforated metal plate with a suspension of an oxidic iron catalyst containing 450 grams of iron, 5 grams of copper, and 1.1 grams of potassium in 4000 grams of liquid paraffin hydrocarbons boiling between 300° C. and 330°C., at a temperature of 270°C. and a gas pressure of 11 atmospheres, a synthesis gas containing CO and H_2 in the ratio of 3:2 and 4-5% of CO_2 at a space velocity of 180 per hour (i.e., 180 Ncbm per cubic metre of the catalyst suspension).

The total products—179 grams—formed at a conversion of 91% of CO per Ncbm of $CO+H_2$, included, apart from higher boiling hydrocarbons and small quantities of alcohols, 20 grams of methane and ethane and 96 grams of hydrocarbons with an olefine content of 84% and having more than 2 carbon atoms in the molecule and boiling up to 200°C. at 760 mm. Hg.

EXAMPLE 2.

A synthesis gas containing CO and H_2 in the ratio of 3:2 and 4—5% of CO_2 was passed upwardly, at a pressure of 11 atmospheres and at a space velocity of 300 per hour (i.e., 300 normal cubic metres per cubic metre of catalyst suspension), through a finely perforated metal plate into the suspension of an oxidic iron catalyst containing 450 grams of iron, 5 grams of copper, and 1.5 grams of potassium in 400 grams of liquid paraffin hydrocarbons boiling between 300° C. and 330°C., in the same reactor as used in Example 1. The synthesis temperature was 270°C.

The total products—182 grams—formed at a conversion of 92% of CO per Ncbm of applied $CO+H_2$, included, apart from higher boiling hydrocarbons and small quantities of alcohols, 18 grams of methane and ethane and 132 grams of hydrocarbons from C_3 up to a boiling limit of 200°C. at 760 mm. Hg., with an olefine content of 84%.

Then, in accordance with the steady decrease in the volume of the catalyst suspension a corresponding quantity of synthesis hydrocarbons boiling within the range 290°-330°C., with an olefine content of 7%, was continuously pumped into the reactor during synthesis, and part of the exit gas, having been cooled down to 15°C. and mixed with fresh synthesis gas in the volume ratio of 1:1 without expansion, was pumped back into the reactor.

The total amount of hydrcarbons obtained was 218-220 grams per Ncbm of synthesis gas used,, containing 16 grams of methane plus ethane and 152 grams of hydrocarbons having more than 2 carbon atoms in the molecule and boiling up to 200°C., 86% of which were olefines.

EXAMPLE 3.

A deposit of oxidic hydrates precipitated at the boil from a common solution of the nitrates of iron, copper and aluminium, and containing these metals in the weight ratio of 100:0.5:0.7, was mixed with 1% of K_2CO_3 after washing, dried at 105°C. in a 1 cm. thick layer and crushed to an average particle size of 3 mm. This catalyst was charged into a vertical, cylinder-type reactor having a height of 5 metres and is equipped with vertical tubes containing a cooling agent for the removal of the reaction heat. Synthesis gas containing 1 volume of CO per 1.2 volumes of H_2 was passed downwardly through the reactor, and part of the exit gas, after having passed the product separator, was pumped back to the synthesis gas inlet where it was mixed with fresh synthesis gas and recycled over the catalyst. The volume ratio of recycled gas to fresh synthesis gas was adjusted to 2.5:1 approximately. Together with the synthesis gas, aliphatic hydrocarbons boiling above 200°C. were introduced from the top of the reactor in a quantity of about 50-200 grams per Ncbm of synthesis gas, to trickle on to the upper layer of the catalyst bed. After separation from the exit gas, the non-converted part of the added hydrocarbons, together with the synthesis products boiling above 200°C., were separated from the lower boiling products and recycled to the reactor as described. The synthesis conditions were: synthesis gas pressure 15 atmospheres, temperature 220°-300°C. The average gas throughout was about 200 normal cubic metres of fresh synthesis gas per cubic metre of catalyst space per hour.

Using a recycle ratio of 1 volume of fresh gas per 2.5 volumes of recycle gas, approximately 88% of the carbon monoxide introduced will react in one synthesis stage, forming 164 grams of organic synthesis products per normal cubic metre of $CO+H_2$ used.

With a simultaneous throughput of 120 grams of aliphatic hydrocarbons of the 200°-450°C. boiling range per Ncbm $CO+H_2$, a total of 264 grams of hydrocarbons was separated from the exit gas, having the following composition:—

C_3-Hydrocarbons	10 grams Ncbm $CO+H_2$, with 88% olefines
C_4-Hydrocarbons	14 grams Ncbm $CO+H_2$, with 87% olefines
Hydrocarbons boiling within the range 25°-200°C.	142 grams Ncbm $CO+H_2$, with 86% olefines
Hydrocarbons boiling above 200°C.	... ... 98 grams Ncbm$CO+H_2$.

In addition, a total of 14 grams of methane, ethane and ethylene was obtained together with 6 grams of water-soluble alcohols.

What we claim is:—

1. A process for the production of liquid hydrocarbons boiling up to 200°C., which comprises contacting a synthesis gas containing 0.5-2 volumes of carbon monoxide to 1 volume of hydrogen with a granular iron catalyst containing an alkali-metal compound (calculated as the alkali-metal monoxide) to the extent of not more than 1% by weight of its total iron content, at a temperature in the range 160° to 350°C. at a pressure in the range 2-150 atmospheres and at a space velocity in the range 30-3000 volumes per volume of catalyst per hour in the presence of aliphatic hydrocarbons which boil above 200°C. and which are liquid under the process conditions, the temperature and pressure being so correlated that the said aliphatic hydrocarbons are cracked.

2. A process for the production of liquid hydrocarbons boiling up to 200°C., which comprises passing a synthesis gas containing 0.5-2 volumes of carbon monoxide to 1 volume of hydrogen through an iron catalyst suspended in aliphatic hydrocarbons having boiling points above 200°C., at a space velocity in the range 30-3000 volumes per volume of catalyst suspension per hour, at a temperature in the range 160°-350°C. and at a pressure in the range 2-150 atmospheres, the catalyst containing an alkali-metal compound (calculated as the alkali-metal monoxide) to the extent of not more than 1% by weight of its total iron content, correlating the temperature and pressure so that the said aliphatic hydrocarbons are cracked, and maintaining the quantity of the aliphatic hydrocarbons in the reaction zone substantially constant by replacing those which have been cracked by aliphatic hydrocarbons boiling above 200°C.

3. A process according to either of the preceding claims, in which the pressure is within the range of 9 to 25 atmospheres.

4. A process according to any of the preceding claims, in which the carbon monoxide/hydrogen gas mixture contains 1.5 volumes of carbon monoxide to 1 volume of hydrogen.

5. A process according to any of the preceding claims, in which exit gases are recycled in a ratio of 1-10 volumes per volume of carbon-monoxide/hydrogen feed.

6. A process for the production of liquid hydrocarbons boiling up to 200°C., substantially as hereinbefore described with reference to Example 1, 2 or 3.

7. A process for the production of liquid hydrocarbons boiling up to 200°C. and consisting mainly of olefines, substantially as hereinbefore described.

8. Liquid hydrocarbons boiling up to 200°C. whenever produced by the process of any of the preceding claims.

EDWARD EVANS & CO.,
14-18, High Holborn, London, W.C.1.
Agents for the Applicants.

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ERRATA

SPECIFICATION No. 709,560.

Page 2, line 34, *for* " much " *read* " such "
Page 2, line 43, *for* " alephatic " *read* " aliphatic "
Page 2, line 83, *for* " grains " *read* " grams "
Page 3, line 8, *after* " atmospheres," *insert* " and with "
Page 3, line 32, *for* " 400 " *read* " 4000 "
Page 3, line 73, *after* " and " *delete* " is "

THE PATENT OFFICE,
4th August, 1954.

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