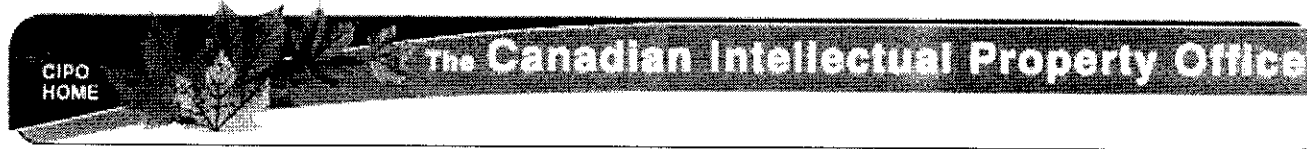




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(54) PROCESS FOR THE PRODUCTION OF LOW BOILING HYDROCARBONS IN THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE

(54) PROCÉDE POUR LA FABRICATION D'HYDROCARBURES A EBULLITION A BASSE TEMPERATURE DANS L'HYDROGENATION CATALYTIQUE D'OXYDE DE CARBONE

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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 additives essential for such synthesis, are well known and established in the art.

One object of the invention is, among others, the production of low-molecular, predominantly unsaturated hydrocarbons in the catalytic hydrogenation of carbon monoxide of the Fischer-Tropsch type.

This and other objects of the invention will be apparent from the following description.

According to the process of the invention a gas mixture containing 0.5-2 volumes of carbon monoxide to one volume of hydrogen, is passed over an iron catalyst having an alkali metal content, calculated as the alkali metal monoxide, of not more than 1% by weight at a temperature of 160° - 350°C. and a pressure of 2-150 atmospheres in the presence of an organic liquid susceptible to cracking under the process conditions, and replacing the organic liquid used up in the reaction by

hydrocarbons of relatively high molecular weight which are liquid under the process conditions.

The preferred alkali metal is potassium and the preferred pressure lies within the range 9-25 atmospheres. 5 The carbon monoxide/hydrogen content of the fresh gas fed to the process should preferably contain about 1.5 volumes of carbon monoxide to every volume of hydrogen.

When proceeding in this manner within the critical operating conditions stated, not only the higher molecular hydrocarbons normally formed in the hydrocarbon synthesis 10 but also the high boiling, i.e., high molecular hydrocarbons which are added during the hydrogenation reaction are converted into low-molecular products of predominantly olefinic character. This conversion to low-molecular 15 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.

20 The process, in accordance with the invention, may be carried out in any conventional synthesis oven or 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 25 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 30 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 pelleted 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 high-molecular hydrocarbon medium. As a still further alternative, the catalyst may be present as a suspension of relatively finely sub-divided 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 less than about 1%. The state of sub-division of such catalyst material and the type of iron catalyst material used should be such and so coordinated that the sub-divided catalyst is comparatively readily wetted by the high-molecular hydrocarbon 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 higher molecular hydrocarbons.

Acyclic paraffins and olefins of natural or synthetic origin and free from catalyst poisons are suitable 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 $250^{\circ}C.$, 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 practice of the invention.

As stated above, the broad operating range of the process, in accordance with the invention, involves pressures ranging between 2 and 150 atm, and temperatures between 160 and 350°C., with a synthesis gas composition of about 0.5-2 volumes of carbon monoxide per volume of hydrogen. For most efficient operation, rates of gas flow are adjusted to correspond to a velocity of between 30 and 3000 Ncbm/hr. per cbm of space filled with catalyst material.

Within the preferred embodiment of the invention, the high yields of low-molecular olefinic hydrocarbons 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 about 200°C. and reintroducing it into the catalytic reaction zone.

The rate of molecular size diminution 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 monoxide. It has been

found, for example, with the synthesis paraffin hydrocarbons boiling above 280°C., that the rate of decomposition is 60 g. and more per normal cubic metre of synthesis gas put through the reactor.

5 Catalytic hydrogenation of carbon monoxide has been carried out in the past in the presence of higher boiling hydrocarbons. In all cases, however, these hydrocarbons were used as an inert liquid medium, which took no part in the synthesis reaction. Though a partial evaporation of
10 the hydrocarbons has been at times resorted to for improving the dispersion of reaction heat and though these hydrocarbons, after being condensed outside the reactor, have been continuously returned into the reactor, no change in molecular size is obtained. This is due to the
15 fact that the reaction conditions and catalysts employed, namely, heavily alkalized catalysts, low synthesis temperatures, and low space velocities will not produce any reduction in molecular size. On the other hand, the so-called hydrogenating decomposition of high molecular
20 hydrocarbons in the presence of hydrogenation catalysts has become known, but differs basically from the process of the invention in that it operates without simultaneous hydrogenation of carbon monoxide, i.e. in the absence of carbon monoxide, and in that the decomposition product
25 contains a high percentage of methane-up to 50% or more.

Therefore, the effect obtained with the process of the invention is the more surprising and could in no way be anticipated. Technically, it is based upon the application of operating conditions and catalyst
30 preparations favouring the predominant formation of low

boiling synthesis products as well as on a sufficiently prolonged residence of the higher molecular hydrocarbons in the contact zone. It is equally impossible to explain the decomposition into predominantly low molecular olefines, as effected by the invention, 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 synthetic product (see H. Koch and 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.

When using iron catalysts, the alkali content, expressed in terms of alkali oxide, 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 g. of iron per litre of catalyst suspension liquid, while the alkali content (expressed as the monoxide) should preferably range between 0.15 and 2 g. per litre of catalyst suspension liquid.

Example 1.

A pressure-resistant reactor, 3 metres in height, is

charged from below through a finely perforated metal plate with a suspension of an oxidic iron catalyst containing 450 g. of iron, 5 g. of copper, and 1.1 g. of potassium in 4000 g. of liquid paraffin hydrocarbons boiling between 300° and 330°C., at a temperature of 270°C. and a gas pressure of 11 atmospheres, and with CO and H₂ in the ratio of 3:2 as well as synthesis gas containing 4-5 % of CO₂ with a space velocity of 180 per hour (i.e., 180 Ncbm per cubic metre of suspension volume).

The total products - 179 g -, formed at a conversion of 91% of CO per Ncbm of applied CO + H₂, include, apart from higher boiling hydrocarbons and small quantities of alcohols, 20 g. of methane and ethane and 96 g. of hydrocarbons with an olefine content of 84% and having more than 2 carbon atoms per molecule and boiling up to 200°C. at 760 mm. Hg. ,

Example 2.

The same reactor as in Example 1 is charged from below through a finely perforated metal plate with the suspension of an oxidic iron catalyst containing 450 g. of iron, 5 g. of copper, and 1.5 g. of potassium in 4000 g. of liquid paraffin hydrocarbons boiling between 300 and 330°C., at a temperature of 270°C. and a gas pressure of 11 atmospheres with CO and H₂ at the ratio of 3:2 as well as synthesis gas containing 4-5% of CO₂ with a space velocity of 300 per hour (i.e., 300 Ncbm per cubic metre of suspension volume).

The total products - 182 g -, formed at a conversion of 92% of CO per Ncbm of applied CO + H₂, include, apart

from higher boiling hydrocarbons and small quantities of alcohols, 18 g. of methane and ethane and 132 g. of hydrocarbons upwards of C_3 up to a boiling limit of $200^{\circ}C.$ at 760 mm. Hg., with an olefine content of 84%.

5 Then, in accordance with the steady decrease in suspension volume, a corresponding quantity of synthesis hydrocarbons boiling within the range $290^{\circ} - 330^{\circ}C.$, with an olefine content of 7%, is continuously pumped into the reactor during synthesis, and part of the exit gas, 10 having been cooled down to $15^{\circ}C.$ and mixed with fresh synthesis gas in the volume ratio of 1:1 without expansion, is pumped back into the reactor.

Total hydrocarbons obtained are 218-220 g. per Ncbm of synthesis gas used, containing 16 g. of methane plus 15 ethane and 152 hydrocarbons having more than 2 15 carbon atoms per mole and boiling up to $200^{\circ}C.$, 86% of which are olefins.

3. A deposit of metal nitrates precipitated at 20 boiling heat from a solution of the nitrates of iron, copper and aluminium. The metals in the weight ratio of 100 : 0.5 : 0.5 were dissolved in K_2CO_3 after washing, dried at $105^{\circ}C.$ in a 25 layer and crushed to an average particle size of 5.

25 In a vertical, cylinder-type reactor having a height of 5 m. which is equipped with vertical tubes containing a cooling agent for the removal of the reaction heat, the reactor is charged from above with synthesis gas containing 1 volume of CO per 1.2 volumes 30 of H_2 , and part of the exit gas, after having passed the

product separator, is pumped back to the synthesis gas inlet where it is mixed with fresh synthesis gas and recycled over the catalyst. The volume ratio of recycled gas to fresh synthesis gas is adjusted to 2.5 : 1 approximately. Together with the synthesis gas, high boiling aliphatic hydrocarbons are introduced from the top of the reactor in a quantity of about 50 - 200 g. per Ncbm of synthesis gas, trickling onto 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. approximately, are separated from the lower boiling products and recycled to the reactor as described. The synthesis conditions are: synthesis gas pressure 15 atmospheres, temperature 220° - 300°C. The average gas throughput is 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 g. of organic synthesis products per normal cubic metre of CO + H₂ used.

With a simultaneous throughput of 120 g. per Ncbm CO + H₂ of aliphatic hydrocarbons of the 200° - 450°C. boiling range, a total of 264 g. of hydrocarbons is separated from the exit gas, having the following composition:-

C ₃ -Hydrocarbons	10 g/Ncbm CO+H ₂ with 88% olefines
C ₄ -Hydrocarbons	14 g/Ncbm CO+H ₂ with 87% olefines

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Hydrocarbons boiling 142 g/Ncbm CO+H₂ with 86% olefines
within the range
25°-200°C.

Hydrocarbons boiling 98 g/Ncbm CO+H₂.
above 200°C.

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

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A process for the production of hydrocarbons of low molecular weight, which comprises contacting a synthesis gas containing 0.5 - 2 volumes of carbon monoxide to 1 volume of hydrogen with a particulate iron catalyst containing an alkali metal compound in an amount, calculated as the alkali metal monoxide, of not more than 1% by weight, the contacting being effected at a temperature within the range 160° - 350°C and at a pressure within the range 2 - 150 atmospheres in the presence of hydrocarbons which are liquid and capable of being cracked under the process conditions, effecting the process in such manner that the said hydrocarbons are cracked, and replacing the hydrocarbons which have been cracked during the reaction by aliphatic hydrocarbons boiling above 200°C .
2. A process for the production of hydrocarbons of low molecular weight, which comprises passing a synthesis gas containing 0.5 - 2 volumes of carbon monoxide to 1 volume of hydrogen over an iron catalyst, in granular or particle form, containing an alkali metal compound to the extent of not more than 1% by weight, the alkali content of the catalyst being calculated as the alkali metal monoxide, at a temperature in the range 160° - 350°C , and a pressure in the range 2 - 150 atmospheres and in the presence of hydrocarbons which are liquid and capable of being cracked under the process conditions, correlating the temperature and pressure conditions

within the said ranges whereby the said hydrocarbons are cracked, and replacing the hydrocarbons which have been cracked during the reaction by aliphatic hydrocarbons boiling above 200°C.

3. A process for the production of a mixture of aliphatic hydrocarbons containing more than two carbon atoms in the molecule and 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 an iron catalyst suspended in aliphatic hydrocarbons having boiling points over 200°C. and being liquid under the process conditions, at a temperature in the range 160° - 350°C. and at a pressure in the range 2 - 150 atmospheres, the iron catalyst containing an alkali metal compound which, calculated as the alkali metal monoxide, comprises not more than 1% by weight of the total iron in the catalyst, recycling exit gases to the contacting zone, and maintaining the quantity of aliphatic hydrocarbons in the contacting zone substantially constant by the addition of aliphatic hydrocarbons having the same characteristics.

4. A process for the synthesis of olefins having boiling points up to 200°C., which comprises contacting, at a temperature in the range 160° - 350°C. and at a pressure in the range 2 - 150 atmospheres, a synthesis gas containing 0.5 - 2 volumes of carbon monoxide to 1 volume of hydrogen with a finely-divided iron catalyst suspended in aliphatic hydrocarbons which boil above 200°C and which are liquid under the synthesis conditions,

the iron catalyst containing an alkali metal compound as promoter which, calculated as the alkali metal monoxide, is present to the extent of not more than 1% by weight of the total iron in the catalyst, recycling exit gases to the synthesis zone whereby the said aliphatic hydrocarbons boiling above 200°C are cracked during the synthesis, and maintaining the quantity of the said aliphatic hydrocarbons in the synthesis zone substantially constant by the addition of aliphatic hydrocarbons having the same characteristics.

5. A process according to any one of claims 2 to 4, in which the pressure is within the range of 9 to 25 atmospheres.

6. A process according to any one of claims 2 to 4, in which the synthesis gas contains about 1.5 volumes of carbon monoxide per volume of hydrogen.

7. A process according to claim 2, in which exit gases are recycled to the reaction zone.

8. A process according to any one of claims 2 to 4, in which exit gases are recycled in a ratio of 1-10 volumes per volume of synthesis gas feed

9. A process according to any one of the claims 2 to 4, in which the space velocity of the synthesis gas mixture is within the range 30-3000 volumes per volume of catalyst suspension medium per hour.