PATENT SPECIFICATION

742,913

Date of Application and filing Complete Specification Nov. 13, 1953.

No. 31616/53.

Application made in Germany on Nov. 13, 1952.

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Index at acceptance :—Classes 2(3), B1G; and 90, K6.

COMPLETE SPECIFICATION

Process for the Synthesis of Hydrocarbons

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, of Homberg, Niederrhein, Germany, a German 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:—

The invention relates to a process for the synthesis of hydrocarbons.

In spite of considerable technical advance, it has hitherto only proved possible economically to carry out the catalytic hydrogenation of carbon monoxide according to the Fischer-Tropsch process and according to the more recent Koelbel-Engelhardt process, by reacting carbon monoxide with steam, when starting gas is particularly cheap and when a very large proportions of the gaseous constituent in the starting gas are utilized.

It is an object of the invention to provide a process for the synthesis of hydrocarbons wherein a cheap starting gas is used and wherein the economic requirements for industrial utilization of a very large proportion of the gaseous constituents may be met.

According to the invention, a process for the synthesis of hydrocarbons by the catalytic hydrogenation of carbon monoxide comprises the use, as starting gas, of blast-furnace gas obtained in the smelting of iron, converting part of the starting gas with steam or adding hydrogen or a carbon monoxide/hydrogen mixture and/or steam to the starting gas contacting the gas mixture so obtained with a carbon monoxide hydrogenation catalyst under conditions of temperature and pressure effective for the synthesis of hydrocarbons, separating hydrocarbons and oxygen-containing organic compounds from the synthesis exit gas to leave an end gas, separating carbon dioxide from the end gas to leave a nitrogen-rich end gas, employing the carbon dioxide so obtained for the treatment of iron or iron ore or for the generation of carbon monoxide for the synthesis, and passing the nitrogen-rich end gas for use in the synthesis of ammonia.

The extensive plants required for the removal of sulphur from the synthesis gas of the Fischer-Tropsch process, are no longer necessary. The blast-furnace gas may either be admixed with a carbon monoxide-hydrogen synthesis gas which is especially prepared for carrying out the Fischer-Tropsch synthesis, or it may be converted in known manner into a gas of a $CO : H_2$ ratio suitable for the Fischer-Tropsch synthesis, by converting part of the CO with steam in a water gas shift reaction, and removal of the CO_2 so formed. It is even more advantageous to use the blast-furnace gas according to the more recent process of Koelbel-Engelhardt directly for the synthesis of hydrocarbons and oxygen containing derivatives thereof after the admixture of steam, thus obviating the use of the much more expensive hydrogen.

In the hydrogenation of carbon monoxide with hydrogen or steam, it has been found to be particularly advantageous to use highly active iron catalysts, because under these reaction conditions the hydrocarbon synthesis proceeds to substantial extent with the formation of carbon dioxide. The carbon dioxide is separated from the synthesis exit gas and is returned to the smelting process, whereby it is reduced to carbon monoxide by reaction with the coke in the blast furnace. The carbon dioxide formed in the hydrocarbon synthesis and separated from the synthesis exit gas, may also be used for the generation of water for use in the hydrocarbon synthesis; in such case reduction of the carbon dioxide to carbon monoxide also occurs in the red-hot coke bed. The carbon dioxide may also be used in iron or steel works, for example for the refining of steel. The removal of the carbon dioxide from the exit gases of the Fischer-Tropsch and Koelbel-Engel-

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hardt syntheses is advantageously effected by washing with water under pressure. When further liquid and gaseous hydrocarbons are withdrawn from the end gas, there remains a nitrogen-rich end gas containing only negligible quantities of carbon dioxide, carbon monoxide, hydrocarbons and hydrogen. This nitrogen-rich end gas, which is completely free from sulphur, is charged to the ammonia synthesis after any small amounts of carbon dioxide and carbon monoxide still present have been removed in known manner. In this manner it is possible to obtain nitrogen-rich gases which contain from 93% to 94% of N_2 and are completely free from sulphur. The amounts of CO_2 removed from the nitrogen-rich gas may be passed to the smelting process as hereinbefore described. The CO obtained in the purification of the nitrogen-rich gas may be passed to the hydrocarbon synthesis together with the blast-furnace gas.

Furthermore, the hydrocarbons of low molecular weight formed in the hydrocarbon synthesis, may be passed to the smelting process.

By carrying out the process hereinbefore described, a practically complete industrial utilisation of all the gaseous constituents present in the blast-furnace gas obtained in the smelting of iron ore, may be secured.

The invention is illustrated in the following example:—

EXAMPLE.

1000 normal cubic metres of blast-furnace gas of the following composition by volume:—

7.0% of CO_2
34.0% of CO
2.0% of H_2
57.0% of N_2

were mixed with 96.4 kilograms of steam and passed at a gauge pressure of from 10 to 20 atmospheres and at a space velocity of approximately 400 to 500 volumes per volume of catalyst per hour, and at a temperature of approximately 250° C. into a reactor suitable for the hydrocarbon synthesis and provided with cooling means. The catalyst in the reactor consisted of approximately 100 parts Fe, 10 parts Cu, 10 parts MgO, 50 parts Kieselguhr, and 4% of K_2CO_3, all by weight.

With a CO conversion of 94%, there were formed in the synthesis 63 kilograms of hydrocarbons containing three or more carbon atoms in the molecule which were removed in known manner by washing under pressure or by adsorption from the exit gas, and 9 kilograms of methane and C_2 hydrocarbons which remained in the end gas.

The end gas, which comprised 920 normal cubic metres, had the following composition by volume:—

31.4% CO_2
2.2% CO
3.3% H_2
1.1% hydrocarbons (C-number 1.5)
62.0% N_2

The carbon dioxide (maximum 288 cubic metres) was scrubbed from this end gas by washing under pressure with water and alkaline media, and was passed to the iron works for use in the smelting process, or in the refining of steel. The washed gas (maximum 630 cubic metres) had the following composition by volume:—

3.2% CO
4.7% H
1.6% hydrocarbons (C-number 1.5)
90.5% N_2

The carbon monoxide was washed out of this gas in known manner with a copper salt solution, and the gas thus obtained (maximum 610 cubic metres) had the following composition by volume:—

93.5% of N_2
4.8% of H_2
1.6% of hydrocarbons

This gas, containing almost 94% of N_2, was absolutely free from sulphur, and could, therefore be passed directly to a known ammonia synthesis. The CO washed out from the gas was added to the blast-furnace gas fed to the hydrocarbon synthesis reactor.

In this manner all of the constitutents of the blast-furnace gas were economically utilized and neither the blast-furnace gas nor the nitrogen gas were subjected to a sulphur-purifying step.

What we claim is:—

1. A process for the synthesis of hydrocarbons by the catalytic hydrogenation of carbon monoxide, which comprises the use, as starting gas, of blast-furnace gas obtained in the smelting of iron, converting part of the starting gas with steam or adding hydrogen or a carbon monoxide/hydrogen mixture and/or steam to the starting gas, contacting the gas mixture so obtained with a carbon monoxide hydrogenation catalyst under conditions of temperature and pressure effective for the synthesis of hydrocarbons, separating hydrocarbons and oxygen-containing organic compounds from the synthesis exit gas to leave an end gas, separating carbon dioxide from the end gas to leave a nitrogen-rich end gas, employing the carbon dioxide so obtained for the treatment of iron or iron ore or for the generation of carbon monoxide for the synthesis, and passing the nitrogen-

rich end gas for use in the synthesis of ammonia.

2. A process according to Claim 1, in which part of the starting gas is converted with steam and the carbon dioxide formed is removed from the mixture.

3. A process according to Claim 1 or Claim 2, in which the carbon monoxide hydrogenation catalyst is an iron catalyst.

4. A process according to any one of the preceding claims, in which the carbon dioxide is separated from the end gas by scrubbing the end gas with water under pressure.

5. A process for the synthesis of hydrocarbons, substantially as hereinbefore described with reference to the example.

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Agents for the Applicants.

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iron or iron ore or for the generation of carbon monoxide for the synthesis, and passing the nitrogen-rich end gas for use in the synthesis of ammonia.

ERRATA

SPECIFICATION NO. 742,913

Page 1, line 90, *after* "water" *insert* "gas".

Page 2, line 2, *for* "wahing" *read* "washing".

THE PATENT OFFICE,
10th February, 1956

DB 31981/1(17)/3486 150 2/56 R

ERRATA

SPECIFICATION No. 742,913

Page 1, line 20, *after* "when" *insert* "the"
Page 1, line 21, *for* "proportions" *read* "proportion"
Page 1, line 21, *delete* "gaseous"
Page 1, lines 21—22, *for* "constitusent" *read* "constituent"
Page 1, line 80, *for* "hydrocarbon" *read* "hydrocarbons"
Page 1, line 90, *after* "water" *insert* "gas"
Page 2, line 2, *for* "wahing" *read* "washing"
Page 2, line 12, *after* "present" *insert* "therein"

THE PATENT OFFICE,
6th July, 1956.

pounds from the synthesis exit gas to leave an end gas, separating carbon dioxide from the end gas to leave a nitrogen-rich end gas, employing the carbon dioxide so obtained for the treatment of

hot coke bed. The carbon dioxide may also be used in iron or steel works, for example for the refining of steel. The removal of the carbon dioxide from the exit gases of the Fischer-Tropsch and Koelbel-Engel-

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