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(54) PROCESS FOR CARRYING OUT THE HYDROCARBON SYNTHESIS WITH COMPLETE UTILIZATION OF ALL THE GASEOUS CONSTITUENTS PRESENT IN THE STARTING GAS

(54) PROCEDE POUR EFFECTUER LA SYNTHESE D'HYDROCARBURE AVEC L'UTILISATION COMPLETE DE TOUS LES COMPOSANTS GAZEUX PRESENTS DANS LE GAZ INITIAL

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The invention relates to a process for the utilization of blast-furnace gas which includes the synthesis of hydrocarbons by the catalytic hydrogenation of carbon monoxide.

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 in which the hydrogenation of the carbon monoxide is effected with steam instead of hydrogen, when the starting gas is particularly cheap and when a very large proportion of the constituents present 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, the starting gas is blast-furnace gas which is obtained in the smelting of iron ores, and the hydrocarbon synthesis is combined with the production of an end gas suitable for use in the synthesis of ammonia. Even at the present time a substantial part of blast-furnace gas evolved in the smelting of iron ores is burnt in waste gas torches or flares, as there is no possibility of completely utilizing such gases in the ironworks. It is immaterial with respect to the utilization of the blast-furnace gas in the process of the present invention whether air or air enriched with oxygen is used as the

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blast in the smelting of the iron ores.

The blast-furnace gas obtained, which consists substantially of carbon monoxide and nitrogen, is suitable for the hydrocarbon synthesis, because due to the nature of the smelting process it is obtained practically free from sulphur, so that the extensive scrubbing units 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.

The gas so obtained then forms the feed gas for the hydrocarbon synthesis, the synthesis conditions, including temperature, pressure, catalyst, ratio of constituents in feed gas, and space velocity, being well known in the art.

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 a substantial extent with the formation of carbon dioxide. The carbon dioxide thus obtained 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. It is also possible to return the carbon dioxide obtained in the hydrocarbon synthesis to the gasifying process of the Fischer-Tropsch synthesis, i.e. to use it for the generation of water gas; 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-Engelhardt syntheses is advantageously effected by washing with water under pressure. When liquid and gaseous hydrocarbons are also separated from the exit gas, there remains a nitrogen-rich gas containing only negligible quantities of carbon dioxide, carbon monoxide, hydrocarbons and hydrogen. This nitrogen-rich gas, which is completely free from sulphur, is fed to the ammonia synthesis after any small amounts of carbon dioxide and carbon monoxide still present therein have been removed in known manner. In this manner it is possible to obtain nitrogen-rich gases which contain 93% to 94% of N_2 and are completely free from sulphur. The amounts of CO_2 removed from the nitrogen-rich

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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 utilization 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,

are 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 consists of approximately 100 parts Fe, 10 parts Cu, 10 parts MgO, 50 parts Kieselguhr, and 4% of K_2CO_3.

With a CO conversion of 94%, there are formed in the synthesis 53 kilograms of C_3 and higher hydrocarbons which are 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 remain in the exit gas.

The exit gas, which comprises 920 normal cubic metres, has 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) is scrubbed out of this end gas by washing under pressure using aqueous alkaline media, and is passed to the smelting process or is used in the refining of steel. The scrubbed gas (maximum 630 cubic metres) has the following composition by volume:-

3.2% CO
4.7% H_2
1.6% hydrocarbons (C-number 1.5)
90.5% N_2

The carbon monoxide is scrubbed from this gas in known manner with a copper salt solution, and the gas thus obtained (maximum 610 cubic metres) has 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, is absolutely free from sulphur, and may, therefore, be passed directly to a known ammonia synthesis. The CO removed by scrubbing is added to the blast-furnace gas which is fed to the hydrocarbon synthesis reactor.

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

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

1. A process for the synthesis of hydrocarbons by the catalytic hydrogenation of carbon monoxide, which comprises converting blast-furnace gas into a mixture suitable for use as a hydrocarbon synthesis feed gas, contacting the feed gas 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, and passing the nitrogen-rich end gas to an ammonia synthesis process.

2. A process for the synthesis of hydrocarbons by the catalytic hydrogenation of carbon monoxide, which comprises contacting a mixture of blast-furnace gas and steam 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,

and passing the nitrogen-rich end gas to an ammonia synthesis process.

3. A process for the synthesis of hydrocarbons by the catalytic hydrogenation of carbon monoxide, which comprises subjecting a mixture of blast-furnace gas and steam to the water-gas shift reaction, adding blast-furnace gas to the product to yield a hydrocarbon synthesis feed gas, contacting the feed gas 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 end gas, separating carbon dioxide from the end gas to leave a nitrogen-rich end gas, and passing the nitrogen-rich end gas to an ammonia synthesis process.

4. A process for the synthesis of hydrocarbons by the catalytic hydrogenation of carbon monoxide, which comprises adding hydrogen to blast-furnace gas to yield a hydrocarbon synthesis feed gas, contacting the feed gas with a carbon monoxide hydrogenation catalyst under conditions of temperature and pressure effective for the synthesis of hydrocarbons,

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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, and passing the nitrogen-rich end gas to an ammonia synthesis process.

5. A process according to claim 3, in which carbon dioxide is removed from the product of the water-gas shift reaction before blast-furnace gas is added to the product.

6. A process according to any one of claims 1, 2 and 3, in which the carbon monoxide hydrogenation catalyst is an iron catalyst.

7. A process according to any one of claims 1, 2 and 3, in which the carbon dioxide is separated from the end gas by scrubbing with water under pressure.

8. A process according to any one of claims 1, 2 and 3, in which the carbon dioxide separated from the end gas is used in the treatment of iron or of iron ore.

9. A process according to any one of claims 1, 2 and 3, in which the carbon dioxide separated from the end gas is employed for the generation of carbon monoxide which is fed to the synthesis.

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