PATENT SPECIFICATION

Application Date: July 15, 1938. No. 6595/39.
(Divided out of Application No. 21086/38).
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518,605

PROVISIONAL SPECIFICATION

Improvements in or relating to the Conversion of Carbon-monoxide with Hydrogen

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) to be as follows:—

In the preparation of liquid hydrocarbons by the conversion of carbon monoxide with hydrogen a marked formation of undesirable low molecular, in particular gaseous hydrocarbons takes place by using very active catalysts. This high formation of gas reduces the yield of the desired liquid products and is therefore undesirable in most cases.

My foreign correspondents have now found that in the said reactions, the formation of undesirable low molecular hydrocarbons can be reduced considerably by adding cyclic hydrocarbons which under the reaction conditions are at least partly vaporous. Both aromatic hydrocarbons and naphthenes may be used. The most suitable substances are low boiling cyclic hydrocarbons of the boiling range of benzines (benzene, toluene, xylene and cyclohexane) and middle oils or products containing the same, such as mineral coal tar middle oil or middle oil from the destructive hydrogenation of mineral coal; substances of high or boiling point may also be added when under the reaction conditions they have such a vapour pressure that they are present to a considerable extent in the vapour form; this is the case for example with naphthalene and its homologues and also with lower boiling mineral coal tar fractions.

The said cyclic hydrocarbons are generally speaking added in amounts of between 10 and 60 per cent. by weight with reference to the throughput of carbonaceous substances. The amount to be added in individual cases depends in particular on the nature of the reaction, on the activity of the catalyst and on the nature of the additional substance. The amounts added are greater in the case of catalysts which tend strongly to form gas than in the case of catalysts having this tendency to a lesser degree.

The cyclic hydrocarbons may be added continuously or at intervals. In the latter case the addition is preferably made when the formation of undesirable low molecular hydrocarbons begins to exceed the desirable degree, which may become evident by the occurrence of great evolution of heat. The additions may also be made at equal intervals of time. When adding the additional substances continuously, the amount added may be constant or variable. The cyclic hydrocarbons may also be added at several places in the reaction chamber. The catalyst may also be laden with cyclic hydrocarbons before use.

When working in the reaction of carbon monoxide with hydrogen for the formation of high boiling hydrocarbon mixtures, the proportion of high molecular products formed may be considerably increased at the expense of the low molecular hydrocarbons, such as benzine, by the addition of cyclic hydrocarbons.

Highly active catalysts having a strong tendency to form gaseous hydrocarbons, in particular methane, are in particular substances containing nickel, as for example those in which the nickel is present in admixture with other catalytically active substances, such as iron, cobalt or the compounds of rare earths, thorium, titanium, copper, zirconium, molybdenum, chromium, tungsten, germanium, manganese or of the alkali or alkaline earth metals, or also with the said metals themselves, and which may also be applied to carriers, such as active silicic acid, alumina, magnesia or zinc oxide. These catalysts containing nickel are prepared in known manner, as for example by reduction from the oxides, the oxalate or carbonate in the presence of reducing gases, such as hydrogen and/or carbon monoxide and at temperatures between

[*Price* 1/-]

200° and 500°, or even at higher temperatures, as for example 700°, 800° or 1000° Centigrade, whereby the substances may be heated until a partial sintering takes place (for example from about 2 to 4 hours at 850° Centigrade).

Even in the case of catalysts containing no nickel, however, the addition of the said cyclic compounds is of advantage. Among such there may be mentioned in particular substances containing iron, as for example iron obtained by the reduction of fused ferrosoferric oxide, which is advantageously provided with additions of other substances such as titanium or silicon or their compounds, or iron obtained by reduction of non-fused iron compounds and simultaneous or subsequent sintering, which likewise may contain additions of other substances.

The same is true for catalysts containing cobalt.

The said reactions of carbon monoxide with hydrogen are carried out under known conditions, namely at temperatures between 150° and 450°, preferably between 180° and 300° Centigrade, at atmospheric or increased pressure, as for example between 5 and 200 atmospheres.

The other conditions, such as time of treatment, relative proportions of the reactants and the like are also as usual. The reactions of carbon monoxide and hydrogen may be carried out in the presence of accompanying gases, such as carbon dioxide or methane. The proportion of the carbon monoxide content to the hydrogen content in the initial gas may vary within a wide range.

The following Example will further illustrate the nature of this invention but the invention is not restricted to this Example.

EXAMPLE.

A gas consisting of carbon monoxide and hydrogen in the ratio of 1:2 is led at 330° Centigrade together with 5 kilograms of sulphur-free benzene vapour per 100 cubic metres of gas under a pressure of 50 atmospheres over a multi-substance catalyst containing mainly nickel. 110 grams of liquid hydrocarbons are obtained per cubic metre of gas; without the addition of benzene the greater part of the reaction products consists of gaseous hydrocarbons.

Dated this 28th day of February, 1939.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields,
London, W.C.2,
Agents.

COMPLETE SPECIFICATION

Improvements in or relating to the Conversion of Carbon-monoxide with Hydrogen

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn, Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany) and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

In the preparation of liquid hydrocarbons by the conversion of carbon monoxide with hydrogen a marked formation of undesirable low molecular, in particular gaseous hydrocarbons takes place by using very active catalysts. This high formation of gas reduces the yield of the desired liquid products and is therefore undesirable in most cases.

My foreign correspondents have now found that in the said reactions the formation of undesirable low molecular hydrocarbons, such as methane, can be reduced considerably by adding cyclic hydrocarbons which under the reaction conditions are at least partly vaporous. Both aromatic hydrocarbons and naphthenes may be used. The most suitable substances are low boiling cyclic hydrocarbons of the boiling range of benzines (benzene, toluene, xylene and cyclohexane) and middle oils or products containing the same, such as mineral coal, tar middle oil or middle oil from the destructive hydrogenation of mineral coal; substances of higher boiling point may also be added when under the reaction conditions they have such a vapour pressure that they are present to a considerable extent in the vapour form; this is the case for example with naphthalene and its homologues and also with lower boiling mineral coal tar fractions.

The said cyclic hydrocarbons are generally speaking added in amounts of between 10 and 60 per cent. by weight with reference to the throughput of carbonaceous substances. The amount to be added in individual cases depends in particular on the nature of the reaction, on the activity of the catalyst and on the nature of the additional substance. The amounts added are greater in the case of catalysts which tend strongly to form gas than in the case of catalysts having this tendency to a lesser degree.

The cyclic hydrocarbons may be added continuously or at intervals. In the latter case the addition is preferably made when the formation of undesirable low molecular hydrocarbons begins to exceed the desirable degree, which may become evident by the occurrence of great evolution of heat. The additions may also be made at equal intervals of time. When adding the additional substances continuously, the amount added may be constant or variable. The cyclic hydrocarbons may also be added at several places in the reaction chamber. The catalyst may also be laden with cyclic hydrocarbons before use.

When working in the reaction of carbon monoxide with hydrogen for the formation of high boiling hydrocarbon mixtures, the proportion of high molecular products formed may be considerably increased at the expense of the low molecular hydrocarbons, such as benzine, by the addition of cyclic hydrocarbons.

Highly active catalysts having a strong tendency to form gaseous hydrocarbons, in particular methane, are in particular substances containing nickel, as, for example, those in which the nickel is present in admixture with other catalytically active substances, such as iron, cobalt or the compounds of rare earths, thorium, titanium, copper, zirconium, molybdenum, chromium, tungsten, germanium, manganese or of the alkali or alkaline earth metals, or also with the said metals themselves, and which may also be applied to carriers, such as active silicic acid, alumina, magnesia, or zinc oxide. These catalysts containing nickel are prepared in known manner, as for example by reduction from the oxides, the oxalate or carbonate in the presence of reducing gases, such as hydrogen and/or carbon monoxide and at temperatures between 200° and 500°, or even at higher temperatures, as for example 700°, 800° or 1000° Centigrade, whereby the substances may be heated until a partial sintering takes place (for example from about 2 to 4 hours at 850° Centigrade).

Even in the case of catalysts containing no nickel, however, the addition of the said cyclic compounds is of advantage. Among such there may be mentioned in particular substances containing iron, as for example iron obtained by the reduction of fused ferrosoferric oxide, which is advantageously provided with additions of other substances, such as titanium or silicon or their compounds, or iron obtained by reduction of non-fused iron compounds and simultaneously or subsequent sintering, which likewise may contain additions of other substances.

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The said reactions of carbon monoxide with hydrogen are carried out under known conditions, namely at temperatures between 150° and 450°, preferably between 180° and 300° Centigrade, at atmospheric or increased pressure, as for example between 5 and 200 atmospheres.

The other conditions, such as time of treatment, relative proportions of the reactants and the like are also as usual. The reactions of carbon monoxide and hydrogen may be carried out in the presence of accompanying gases, such as carbon dioxide or methane. The proportion of the carbon monoxide content to the hydrogen content in the initial gas may vary within a wide range.

The following Example will further illustrate how the said invention may be carried out in practice but the invention is not restricted to the Example.

EXAMPLE.

A gas consisting of carbon monoxide and hydrogen in the ratio of 1:2 is led at 330° Centigrade together with 5 kilograms of sulphur-free benzene vapour per 100 cubic metres of gas under a pressure of 50 atmospheres over a multi-substance catalyst containing mainly nickel. 110 grams of liquid hydrocarbons are obtained per cubic metre of gas; without the addition of benzene the greater part of the reaction products consists of gaseous hydrocarbons.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process for the production of valuable liquid hydrocarbons by catalytic conversion of carbon monoxide with hydrogen, which comprises working with an addition of cyclic hydrocarbons which under the reaction conditions are vaporised at least to a substantial extent.

2. In the process as claimed in claim 1, adding low boiling cyclic hydrocarbons boiling within the boiling point range of benzines and/or middle oils.

3. In the process as claimed in claims 1 or 2, adding the cyclic hydrocarbons after intervals, particularly at moments when the formation of low boiling hydrocarbons becomes undesirably large.

4. In the process claimed in claims 1 or

2, adding the cyclic hydrocarbons periodically.

5. In the process as claimed in claims 1 or 2, continuously adding the cyclic hydrocarbons while varying the amount of the additions.

6. In the process as claimed in any of claims 1 to 5, adding the cyclic hydrocarbons at several points into the reaction space.

7. Liquid hydrocarbons when prepared by the process particularly described and ascertained.

Dated this 1st day of March, 1939.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

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