AMENDED SPECIFICATION.

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PATENT SPECIFICATION

Application Date: Sept. 15, 1927. No. 24,322/27.

301,969

Complete Left: June 8, 1928.

Complete Accepted: Dec. 13, 1928.

PROVISIONAL SPECIFICATION.

Improvements in and Apparatus for the Catalytic Conversion of Hydrocarbons.

I, JAMES YATE 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 the I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany) to be as follows:—

It has already been proposed to convert hydrocarbons into mixtures of carbon monoxide and hydrogen, by passing them together with water vapour or carbon dioxide with or without the addition of air or oxygen or both over catalysts, at elevated temperatures. These reactions are, as is well known, highly endothermic, and as they only take place at elevated temperatures, it is difficult to heat the reacting materials to the required extent.

My foreign correspondents have now found that no difficulties are encountered in carrying out the process, if the contact substances, for example nickel activated with alumina, be arranged in long chambers having a large heating surface and being so arranged that the heating medium does not come into direct contact with the catalyst. The walls of the said chamber consist of a material of high heat conductivity which is resistant to high temperatures, for example highly alloyed steels, especially chromium nickel steel or high-grade nickel alloys, such as chromium nickel. Under these conditions the process may be carried out at temperatures below 1000° Centigrade. As long chambers there may be employed, for example, tubes with not too large a cross-sectional area, for instance with a cross-sectional area of 100 square centimetres or less. For example a reaction vessel similar to a tube boiler may be employed, and the contact substances may be arranged either within the tubes, in which case a heating medium, for example hot combustion gases, is conducted through the space surrounding the tubes, or the heating gases are conducted through the tubes of the said reaction vessel, similar to a tube boiler in which case the catalyst is arranged in the long narrow spaces formed by the tubes within the whole vessel.

In an apparatus according to this invention given by way of example, the contact mass is arranged in a system of tubes contained in an elongated reaction chamber to which tubes the hydrocarbons are admitted by a supply pipe. Pipes are also provided for admitting steam and carbon dioxide, air or oxygen, respectively, to the said tubes. Hot combustion gases from a suitable burner are passed between the said tubes, which gases leave the said chamber at the end opposite to which they entered, the steam or other gases entering passing through and leaving the catalyst tubes in a similar course.

When using not activated contact substances, and in the case of very impure initial gases or vapours, it is beneficial to work with the hydrocarbons and the heating medium in a counter current. But when employing activated contact substances, for example catalysts activated by alumina, and pure initial substances, it is best to pass the gases in the same direction as the heating medium. If mainly hydrogen and no carbon monoxide is to be produced, such catalysts as accelerate the conversion of carbon monoxide by means of steam, for example catalysts containing iron oxide and chromium oxide, may be mixed with the whole of the contact mass or only with the latter part of the same.

If the initial substances are very much

polluted, especially with organic compounds of sulphur, these must be removed, which may be effected, for example, by passing the gas over a metallic mass which absorbs the compounds of sulphur, for example copper, or over a contact substance which converts the organic sulphur compounds into hydrogen sulphide, for example over metal oxides heated to about 300° Centigrade, and removing the hydrogen sulphide in any suitable manner, or according to any other known or suitable process.

Other gases, especially oxygen or air, may also be added to the mixture of hydrocarbons and steam or carbon dioxide, and the process may also be carried out in two stages in accordance with the specification of our copending application No. 28,747 A.D. 1926, the reacting materials being in the first stage subjected to partial combustion at high temperatures, if desired with the addition of steam, in such a manner, that the resulting gas mixture still contains an appreciable amount of hydrocarbons, and this mixture is then completely converted in the second stage in the manner described above at a lower temperature.

The following examples will further illustrate the nature of this invention, but the invention is not limited to these examples.

EXAMPLE 1.

50 cubic metres of illuminating gas containing about 3 per cent of carbon dioxide, 2 per cent of heavy hydrocarbons, 6 per cent of carbon monoxide, 52 per cent of hydrogen, 31 per cent of methane and 6 per cent of nitrogen, are passed with about 100 kilograms of steam, preferably superheated, over a contact mass consisting of nickel activated with alumina, which is arranged in tubes of a highly alloyed steel externally heated to between 800° and 900° Centigrade. A gas consisting of about 14.5 per cent of carbon dioxide, 78 per cent of hydrogen, 4.6 per cent of carbon monoxide, 0.2 per cent of methane and 2.7 per cent of nitrogen is obtained.

EXAMPLE 2.

Illuminating gas which has been freed from hydrogen sulphide and benzene and is saturated with water vapour is passed at 400° Centigrade over a catalyst containing iron oxide and chromium oxide and the hydrogen sulphide thus produced from the organic sulphur compounds is removed by means of active charcoal. A gas is thus obtained having approximately the following composition: 3 per cent of carbon dioxide, 2 per cent of heavy hydrocarbons, 6 per cent of carbon monoxide, 52 per cent of hydrogen, 31 per cent of methane and 6 per cent of nitrogen. This mixture is allowed to react at about 600° Centigrade, in the presence of a nickel catalyst activated with alumina with from two to three times the amount of steam necessary for the decomposition of the methane, the said catalyst being arranged in externally heated tubes of highly alloyed steel, and then contains approximately: 14.5 per cent of carbon dioxide, 78.0 per cent of hydrogen, 4.6 per cent of carbon monoxide, 0.2 per cent of methane and 2.7 per cent of nitrogen.

EXAMPLE 3.

Illuminating gas, which has been freed from hydrogen sulphide and benzene, is passed over iron oxide activated with chromium oxide at 300° Centigrade in order to remove the organic compounds of sulphur. The gas mixture thus obtained is then passed in admixture with from two to three times the amount of steam necessary for the decomposition of the methane over a nickel catalyst activated with alumina, the said catalyst being arranged in a long reaction vessel made of highly alloyed chromium-nickel steel, which vessel is traversed longitudinally by a large number of tubes presenting a large surface area. Heating gases are passed through the said tubes and the catalyst is thus maintained at a temperature of from 700° to 800° Centigrade. The said gas mixture is thus converted into a mixture having the following composition: 12.6 per cent of carbon dioxide, 77.5 per cent of hydrogen, 7.0 per cent of carbon monoxide, 0.2 per cent of methane and 2.7 per cent of nitrogen. If the organic compounds of sulphur are not previously removed, the employment of temperatures of about 1000° Centigrade is necessary under like conditions in order to obtain a satisfactory conversion.

EXAMPLE 4.

44 cubic metres of illuminating gas containing about 30 per cent of hydrocarbons are subjected to partial combustion with 11 cubic metres of oxygen and 12 kilograms of steam. The resulting gas which contains about 8 per cent of carbon dioxide, 60 per cent of hydrogen, 19 per cent of carbon monoxide, 7 per cent of methane and 6 per cent of nitrogen, is then passed together with 18 kilograms of steam through the tube system, as described in Example 2, filled with a nickel contact mass and heated to 600° Centigrade, whereby a gas mixture containing 20 per cent of carbon dioxide, 72 per cent of hydrogen, 3.6 per cent of carbon monoxide, 0.4 per cent of methane and 4 per cent of nitrogen is obtained.

Dated this 15th day of September, 1927.

JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London, W.C. 2,
Agents.

COMPLETE SPECIFICATION (AMENDED).

Improvements in and Apparatus for the Catalytic Conversion of Hydrocarbons.

I, JAMES YATE 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:—

It has already been proposed to convert hydrocarbons into gases comprising hydrogen or mixtures of carbon monoxide and hydrogen, by passing them together with water vapour or carbon dioxide with or without the addition of air or oxygen or both over catalysts, at elevated temperatures. These reactions are, as is well known, highly endothermic, and as they only take place at elevated temperatures, it is difficult to heat the reacting materials to the required extent.

My foreign correspondents have now found that no difficulties are encountered in carrying out the process, if the catalyst, for example nickel activated with alumina, be arranged in elongated chambers having a large heating surface and being so arranged that the heating medium does not come into direct contact with the catalyst, which is moreover of different material from that of the walls of the said chambers. The heating walls of the said chamber consist of a material of high heat conductivity which is resistant to high temperatures, for example highly alloyed steels, especially chromium nickel steel or high-grade nickel alloys, such as chromium nickel. Under these conditions the process is carried out at temperatures arranged between about 600° and 1000° Centigrade, the heating by means of the heating medium being carried out throughout the reaction. As elongated chambers there may be employed, for example, tubes with not too large cross-sectional area, for instance with a cross-sectional area of 100 square centimetres or less, and having, for example, a length of about 1 to 4 metres. For example a reaction vessel similar to a tube boiler may be employed and the contact substances may be arranged either within the tubes, in which case a heating medium, for example hot combustion gases, is conducted through the space surrounding the tubes, or the heating gases are conducted through the tubes of the said reaction vessel, similar to a tube boiler, in which case the catalyst is arranged in the long narrow spaces, formed by the tubes within the whole vessel.

In the accompanying diagrammatic drawing an apparatus according to this invention is illustrated in vertical section, by way of example, to which however the invention is not limited.

The contact mass is arranged in a system of tubes to which the hydrocarbons are admitted at B. Pipes C and D serve for admitting steam and carbon dioxide, air or oxygen, respectively. Tubes A are arranged in a vessel E through which hot combustion gases from a burner F are passed, which leave the vessel E at G. The gases leaving the catalyst tubes A are discharged at H.

When using non-activated contact substances, and in the case of very impure initial gases or vapours, it is beneficial to work with the hydrocarbons and the heating medium in a counter current. But when employing activated contact substances, for example catalysts activated by alumina, and pure initial substances, it is best to pass the gases in the same direction as the heating medium. If mainly hydrogen and no carbon monoxide is to be produced, such catalysts as accelerate the conversion of carbon monoxide by means of steam, for example catalysts containing iron oxide and chromium oxide, may be mixed with the whole of the contact mass or only with the latter part of the same.

If the initial substances are very much polluted, especially with organic compounds of sulphur, these must be removed, which may be effected, for example, by passing the gas over a metallic mass which absorbs the compounds of sulphur, for example copper, or over a contact substance which converts the organic sulphur compounds into hydrogen sulphide, for example over metal oxides heated to about 300° Centigrade, and removing the hydrogen sulphide in any suitable manner, or according to any other known or suitable process.

Other gases, especially oxygen or air, may also be added to the mixture of hydrocarbons and steam or carbon dioxide. The process may be carried out in two stages in accordance with Specification No. 288,662, the reacting materials being in the first stage subjected to partial combustion at high temperatures, if desired with the addition of steam, in such a manner, that the resulting gas mixture still contains an appreciable amount of hydrocarbons, and this mixture is then completely converted in the second stage in the manner described above at a lower temperature.

The following Examples will further illustrate how the invention may be carried into practical effect, but the invention is not limited to these Examples.

EXAMPLE 1.

50 cubic metres of illuminating gas containing about 3 per cent of carbon dioxide, 2 per cent of heavy hydrocarbons, 6 per cent of carbon monoxide, 52 per cent of hydrogen, 31 per cent of methane and 6 per cent of nitrogen, are passed with about 100 kilograms of steam, preferably superheated, over a contact mass consisting of nickel activated with alumina, which is arranged in tubes of a highly alloyed steel externally heated to between 800° and 900° Centigrade. A gas consisting of about 14.5 per cent of carbon dioxide, 78 per cent of hydrogen, 4.6 per cent of carbon monoxide, 0.2 per cent of methane and 2.7 per cent of nitrogen is obtained.

EXAMPLE 2.

Illuminating gas which has been freed from hydrogen sulphide and benzene and is saturated with water vapour is passed at 400° Centigrade over a catalyst containing iron oxide and chromium oxide and the hydrogen sulphide thus produced from the organic sulphur compounds is removed by means of active charcoal. A gas is thus obtained having approximately the following composition: 3 per cent of carbon dioxide, 2 per cent of heavy hydrocarbons, 6 per cent of carbon monoxide, 52 per cent of hydrogen, 31 per cent of methane and 6 per cent of nitrogen. This mixture is allowed to react at about 600° Centigrade, in the presence of a nickel catalyst activated with alumina with two to three times the amount of steam necessary for the decomposition of the methane, the said catalyst being arranged in externally heated tubes of highly alloyed steel, and then contains approximately: 14.5 per cent of carbon dioxide, 78.0 per cent of hydrogen, 4.6 per cent of carbon monoxide, 0.2 per cent of methane and 2.7 per cent of nitrogen.

EXAMPLE 3.

Illuminating gas, which has been freed from hydrogen sulphide and benzene, is passed over iron oxide activated with chromium oxide at 300° Centigrade in order to remove the organic compounds of sulphur. The gas mixture thus obtained is then passed in admixture with from two to three times the amount of steam necessary for the decomposition of the methane over a nickel catalyst activated with alumina, the said catalyst being arranged in a long reaction vessel made of highly alloyed chromium-nickel steel, which vessel is traversed longitudinally by a large number of tubes presenting a large surface area. Heating gases are passed through the said tubes and the catalyst is thus maintained at a temperature of from 700° to 800° Centigrade. The said gas mixture is thus converted into a mixture having the following composition: 12.6 per cent of carbon dioxide, 77.5 per cent of hydrogen, 7.0 per cent of carbon monoxide, 0.2 per cent of methane and 2.7 per cent of nitrogen. If the organic compounds of sulphur are not previously removed, the employment of a temperature of about 1000° Centigrade is necessary under like conditions in order to obtain a satisfactory conversion.

EXAMPLE 4.

44 cubic metres of illuminating gas containing about 30 per cent of hydrocarbons are subjected to partial combustion with 11 cubic metres of oxygen and 12 kilograms of steam. The resulting gas which contains about 8 per cent of carbon dioxide, 60 per cent of hydrogen, 19 per cent of carbon monoxide, 7 per cent of methane and 6 per cent of nitrogen, is then passed together with 18 kilograms of steam through the tube system, as described in Example 2, filled with a nickel contact mass and heated to 600° Centigrade, whereby a gas mixture containing 20 per cent of carbon dioxide, 72 per cent of hydrogen, 3.6 per cent of carbon monoxide, 0.4 per cent of methane and 4 per cent of nitrogen is obtained.

I am aware of British Patent Specifications Nos. 12,608/88, 12,978/13, 163,703 and 274,610, and of No. 267,535 as laid open to public inspection under sub-section 3 (a) of Section 91 of the Patents Acts. I am also aware of German Patent Specifications Nos. 306,301 and 411,389. It is to be understood that I make no claim to anything described in the aforesaid specifications.

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 of producing gases comprising hydrogen or mixtures of hydrogen with carbon monoxide which consists in bringing hydrocarbons together with water vapour or carbon dioxide with or without an addition of air or oxygen or both into contact with catalysts arranged in elongated chambers, having large heating surfaces and heated throughout the reaction to temperatures arranged between about 600° and 1000° Centigrade by means of a heating medium which does not come into direct contact with the catalyst, the heated walls of the said chambers consisting of a material of high heat conductivity which is resistant to high temperatures and the catalyst being of different material from that of the heated walls.

2. In carrying out the process claimed in claim 1, freeing initial hydrocarbons which are polluted, especially with organic compounds of sulphur, from their impurities prior to the conversion of the said hydrocarbons.

3. A specific method of carrying out the processes claimed in claims 1 and 2 which consists in operating in two stages in such a manner that in the first stage a mixture is obtained still containing appreciable amounts of hydrocarbons, and carrying out the said second stage according to Claims 1 and 2.

4. The process of producing gases comprising hydrogen or mixtures of hydrogen with carbon monoxide, substantially as described in each of the foregoing Examples.

5. Apparatus for carrying out the process claimed in claims 1, 2, 3 and 4, substantially as hereinbefore described and illustrated in the accompanying drawing.

6. Gases comprising hydrogen or mixtures of hydrogen with carbon monoxide when obtained in accordance with the processes claimed in the preceding claiming clauses.

Dated this 8th day of June, 1928.

JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London, W.C. 2,
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[This Drawing is a reproduction of the Original on a reduced scale]