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AMENDED SPECIFICATION

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PATENT SPECIFICATION

Application Date: July 14, 1936. No. 19561/36.

478,318

Complete Specification Left: June 18, 1937.

Complete Specification Accepted: Jan. 14, 1938.

1291

PROVISIONAL SPECIFICATION

Improvements in the Conversion of Carbon Monoxide with Hydrogen into Hydrocarbons or their Oxygen-containing Derivatives

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 conversion of carbon monoxide with hydrogen to form hydrocarbons or their derivatives, such as alcohols and acids, at elevated temperatures and in the presence of catalysts, the great heat of reaction offers difficulties because it can only be led away by means of troublesome measures and at temperatures higher than the proper reaction temperature a decomposition of the carbon monoxide into carbon dioxide and carbon (occurring in combination with a strong formation of methane) may readily take place, especially when using catalysts containing iron, nickel or cobalt, and this may readily lead to stoppage of the plant.

My foreign correspondents have now found that the said difficulties are reduced considerably and that, contrary to expectation, a very high, almost theoretical yield of hydrocarbons liquid at ordinary temperature and their derivatives are obtained by taking care that the gas supplied to the reaction chamber has a considerable content of one or more gases other than carbon monoxide or hydrogen, preferably gases which have no reducing action under the working conditions. As such accompanying gases may be mentioned in particular carbon dioxide and methane which may also be used together with other gases, as for example nitrogen. Other gases may, however, also be used instead of carbon dioxide and/or methane. The amount of the accompanying gases in the gas supplied to the reaction chamber is usually more than 20 per cent. and advantageously more than 40 per cent., for example up to from about 80 to 90 per cent.

The desired concentration of accompanying gases may be maintained in many cases by leading the gas through the reaction chamber several times and, after each exit, separating only the constituents which are liquid at a temperature between 0° and 50° Centigrade. In this way the carbon dioxide formed in the reaction, the formation of which instead of water may be promoted by maintaining certain conditions as regards catalyst, temperature and the like, remains for the greater part in the circulating gas up to a certain concentration dependent on the separation conditions. When this concentration is exceeded, it dissolves to an increased extent in the water also formed or is finally separated in the liquid form, especially when working under increased pressure. When there is insufficient formation of accompanying gases, such gases may be added externally to the circulating gas or to the fresh gas. When the concentration of gases which are not readily separated, such as nitrogen or methane, becomes too great, a part of the circulating gas may be branched off and freed from the accompanying gases.

The said process is of special advantage in the preparation of liquid hydrocarbons from mixtures of carbon monoxide and hydrogen under increased pressure and in the presence of catalysts containing metals of the 8th group of the periodic system of elements, in particular iron. In the presence of the said accompanyng gases, the reaction of carbon monoxide and hydrogen proceeds for the most part with the formation of hydrocarbons and carbon dioxide according to the equation:—

$$2x\mathrm{CO} + x\mathrm{H}_2 = (\mathrm{CH}_2)_x + x\mathrm{CO}_2,$$

but water is also formed according to the equation:—

$$x\mathrm{CO} + 2x\mathrm{H}_2 = (\mathrm{CH}_2)_x + x\mathrm{H}_2\mathrm{O}.$$

For the reaction chamber there may be used a simple tube of suitable material in which the catalyst is distributed, preferably in thin layers in order to allow the gas to pass through easily. The reaction chamber may be provided with a suitable heating for initiating the reaction. Connected to the reaction chamber, if desired after a heat exchanger, is a cooler which cools the gas and also condenses the hydrocarbons liquid at ordinary temperature and the water and a little carbon dioxide. An attached gas-circulating pump conveys the gas back into the reaction chamber, if desired through a heat exchanger and/or a special heating device. The reaction temperature lies between 150° and 500°, preferably between 200° and 400° Centigrade. It is advantageous to use increased pressures of, for example, 5, 10, 20, 50 or 100 to 300 or 500 or more atmospheres.

The circulating gas leaving the reaction chamber, which carries the excess of the heat of reaction with it, consists to a great extent of carbon dioxde and also contains olefines, methane and its homologues, nitrogen, steam and unchanged carbon monoxide and hydrogen.

A special advantage of the process according to this invention consists in the fact that the fresh gas may have a high content of carbon monoxide, as for example from 40 to 70 per cent., and a smaller content of hydrogen than usual, as for example from 60 to 30 per cent., so that the ratio of carbon monoxide to hydrogen need not be 1:2 as usual.

The following Example will further illustrate the nature of this invention but the invention is not restricted to this Example. The parts and percentages are by volume.

EXAMPLE.

A high-pressure tube having an internal diameter of 80 millimetres and a height of 1 metre, which is externally heated and in which a catalyst consisting of ferrosoferric oxide with an addition of uranium, titanium and potassium compounds (prepared by melting iron powder together with titanium oxide, uranyl nitrate and potassium hydroxide in the proportions by weight of 1000:50:50:5 in a stream of oxygen and reducing with hydrogen at 400° Centigrade in the reaction chamber under a pressure of 150 atmospheres) is distributed in 30 layers, serves as the reaction chamber. Behind the reaction chamber there is arranged a cooler and beneath this a separator for the liquid products. To the gas outlet of the separator there is attached a circulating pump which returns the residual gas to the reaction chamber.

As the fresh gas there is introduced behind the circulating pump a mixture of about 3 parts of carbon monoxide and 2 parts of hydrogen containing about 0.5 per cent. of nitrogen. In the whole plant an increased pressure of about 100 atmospheres is maintained; the temperature in the reaction chamber is between about 265° and 300° Centigrade. The circulating gas is charged through the reaction chamber at a speed of about 4 cubic metres (calculated under normal conditions) per hour.

The gas introduced into the reaction chamber has the following composition:—

CO_2	51.0	per	cent.
$\mathrm{C}_n\mathrm{H}_{2n}$	2.5	,,	,,
CO	22.0	,,	,,
H_2	10.0	,,	,,
CH_4 and homologues	12.0	,,	,,
N_2	3.0	,,	,,

The 12 per cent. of methane and homologues consists to the extent of about 20 per cent. of homologues.

A very high content of accompanying gases is thus maintained according to this Example. The liquid products withdrawn per day consist of 2270 cubic centimetres of oil which according to elementary analysis contains 82.2 per cent. of carbon, 13.1 per cent. of hydrogen, 0.1 per cent. of nitrogen and 4.6 per cent. of oxygen. 55 per cent. of the liquid product boils between 40° and 200° Centigrade and the remaining 45 per cent. between 200° and 350° Centigrade. There are also obtained 750 cubic centimetres of acid-reacting water containing about 7.5 per cent. of alcohols. In order to remove any excess of accompanying gases, about 1.2 cubic metres per day are withdrawn from the circulating gas. By the separation of the liquid products, carbon dioxide dissolved therein is also removed.

When working in the manner described only 140 litres or from about 92 to 110 grams of methane and gaseous homologues are formed per 2270 cubic centimetres or 1800 grams of oil; i.e. the formation of methane and gaseous homologues are formed per 2270 cubic centi- of the formation of oil or the conversion of the mixture of carbon monoxide and hydrogen into valuable liquid products amounts to 94 per cent. This is a value which has never been attained by the processes hitherto known.

Dated this 14th day of July, 1936.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

COMPLETE SPECIFICATION

Improvements in the Conversion of Carbon Monoxide with Hydrogen into Hydrocarbons or their Oxygen-containing Derivatives

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), and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

The present invention relates to the production of hydrocarbons containing more than two carbon atoms in the molecule, and more particularly liquid hydrocarbons, or liquid or solid oxygen-containing derivatives of hydrocarbons from carbon monoxide and hydrogen.

The conversion of carbon monoxide with hydrogen to form the said hydrocarbons or their oxygen-containing derivatives at elevated temperatures under superatmospheric pressures, and in the presence of catalysts, leads to a great development of heat which offers difficulties because it can only be led away by means of troublesome measures, while at temperature above the proper reaction temperature a decomposition of the carbon monoxide into carbon dioxide and carbon (conjointly with a strong formation of methane) may readily occur, especially when using catalysts containing iron, nickel or cobalt, and this may readily lead to stoppage of the plant.

My foreign correspondents have now found that the said difficulties are reduced considerably and that, contrary to expectation, a very high, almost theoretical yield of hydrocarbons liquid at ordinary temperature and their oxygen-containing derivatives (such as alcohols, aldehydes, acids and the like) are obtained by providing that the gas supplied to the reaction chamber has a considerable content of carbon dioxide, if desired together with further gases other than carbon monoxide or hydrogen, preferably gases which have no reducing action under the working conditions, the content of hydrogen in the mixture being less than the content of carbon monoxide. In addition to carbon dioxide methane may for example be used as further gas. The amount of the accompanying gases in the gas supplied to the reaction chamber is more than 40 per cent., for example up to from about 80 to 90 per cent.

The desired concentration of accompanying gases may be maintained by leading the gas through the reaction chamber several times, and, after each exit, separating only the constituents which are liquid at a temperature between 0° and 50° Centigrade and under a pressure of about 100 atmospheres. In this way the carbon dioxide formed in the reaction, the formation of which instead of water may be promoted by maintaining certain conditions as regards catalyst, temperature and the like, remains for the greater part in the circulating gas up to a certain concentration dependent on the separation conditions. The unconverted gas and the accompanying gas need not be recycled completely to the reaction space. Also the recirculation of only part of these gases is in many cases advantageous. Again, the said gases need not be recycled to the same reaction space; when operating in several spaces the gases issuing from one space may also be supplied to another space. When the concentration of carbon dioxide is exceeded, it dissolves to an increased extent in the water also formed or is finally separated in the liquid form, especially when working under increased pressure. Thus with carbon dioxide a desired concentration of the accompanying gas may be maintained in a very simple manner. When there is insufficient formation of accompanying gases, such gases may be added as such to the circulating gas or to the fresh gas. When the concentration of gases which are not readily separated, such as nitrogen or methane, becomes too great, a part of the circulating gas may be branched off and freed from the accompanying gases.

The said process is of special advantage in the preparation of liquid hydrocarbons from mixtures of carbon monoxide and hydrogen under increased pressure and in the presence of catalysts containing metals of the 8th group of the periodic system of elements, in particular iron. In the presence of the said accompanying gases, the reaction of carbon monoxide and hydrogen proceeds for the most part with the formation of hydrocarbons and carbon dioxide according to the equation:—

$$2xCO + xH_2 = (CH_2)_x + xCO_2,$$

but water is also formed according to the equation:—

$$xCO + 2xH_2 = (CH_2)_x + xH_2O.$$

For the reaction chamber there may be used a simple tube of suitable material in which the catalyst is distributed, preferably in thin layers in order to allow the gas to pass through easily. The reaction chamber may be provided with a suitable heating for initiating the reaction. Connected to the reaction chamber, if desired after a heat exchanger, is a cooler which cools the gas and also condenses the hydrocarbons liquid at ordinary temperature and the water and a little carbon dioxide. An attached gas-circulating pump conveys the gas back into the reaction chamber, if desired through a heat exchanger and/or a special heating device. The reaction temperature lies between 150° and 500°, preferably between 200° and 400° Centigrade. The pressure employed must be higher than 5 atmospheres, and pressures of 10, 20, 50 or 100 to 300 or 500 or more atmospheres may be employed.

The circulating gas leaving the reaction chamber, which carries the excess of the heat of reaction with it, consists to a great extent of carbon dioxide and also contains olefines, methane and its homologues, nitrogen, steam and unchanged carbon monoxide and hydrogen.

A special advantage of the process according to this invention consists in the fact that the fresh gas supplied to the reaction chamber in addition to the circulating gas may have a high content of carbon monoxide, as for example from 40 to 70 per cent., and a smaller content of hydrogen than usual, as for example from 60 to 30 per cent., preferably from less than 50 to 30 per cent., so that the ratio of carbon monoxide to hydrogen need not be 1:2 as usual.

The following Example will further illustrate how the said invention may be carried out in practice but the invention is not restricted to this Example. The parts and percentages are by volume.

EXAMPLE.

A high-pressure tube having an internal diameter of 80 millimetres and a height of 1 metre, which is externally heated and in which a catalyst consisting of ferrosoferric oxide with an addition of uranium, titanium and potassium compounds (prepared by melting iron powder together with titanium oxide, uranyl nitrate and potassium hydroxide in the proportions by weight of 1000:50;50;5 in a stream of oxygen and reducing with hydrogen at 400° Centigrade in the reaction chamber under a pressure of 150 atmospheres) is distributed in 30 layers, serves as the reaction chamber. Behind the reaction chamber there is arranged a cooler and beneath this a separator for the liquid products. To the gas outlet of the separator there is attached a circulating pump which returns the residual gas to the reaction chamber.

As the fresh gas there is introduced behind the circulating pump a mixture of about 3 parts of carbon monoxide and 2 parts of hydrogen containing about 0.5 per cent. of nitrogen. In the whole plant an increased pressure of about 100 atmospheres is maintained; the temperature in the reaction chamber is between about 265° and 300° Centigrade. The circulating gas is charged through the reaction chamber at a speed of about 4 cubic metres (calculated under normal conditions) per hour.

The gas introduced into the reaction chamber has the following composition:—

CO_2	51.0	per cent.
C_nH_{2n}	2.5	,, ,,
CO	22.0	,, ,,
H_2	10.0	,, ,,
CH_4 and homologues	12.0	,, ,,
N_2	3.0	,, ,,

The 12 per cent. of methane and homologues consists to the extent of about 20 per cent. of homologues.

A very high content of accompanying gases is thus maintained according to this Example. The liquid products withdrawn per day consist of 2270 cubic centimetres of oil which according to elementary analysis contains 82.2 per cent. of carbon, 13.1 per cent. of hydrogen, 0.1 per cent. of nitrogen and 4.6 per cent. of oxygen. 55 per cent. of the liquid product boils between 40° and 200° Centigrade and the remaining 45 per cent. between 200° and 350° Centigrade. There are also obtained 750 cubic centimetres of acid-reacting water containing about 7.5 per cent. of alcohols. In order to remove any excess of accompanying gases, about 1.2 cubic metres per day are withdrawn from the circulating gas. By the separation of the liquid products, carbon dioxide dissolved therein is also removed.

When working in the manner described only 140 litres or from about 92 to 110 grams of methane and gaseous homologues are formed per 2270 cubic centimetres or 1800 grams of oil; i.e., the formation of methane and gaseous homologues amounts to only about 6 per cent. of the formation of oil or the conversion of the mixture of carbon monoxide and hydrogen into valuable liquid products amounts to 94 per cent. This is a value which has never been attained by the processes hitherto known.

I am aware that processes have already been proposed in Specifications Nos. 337,409 and 338,854 for the production of oxygenated organic compounds from reacting gases of varying composition, for example reacting gases containing two volumes of carbon monoxide or dioxide to one volume of hydrogen, or equal volumes of carbon monoxide or dioxide and of hydrogen. Mixtures of carbon monoxide and dioxide can also be employed. These proposals do not however, suggest the use of an excess of carbon monoxide over the hydrogen together with the simultaneous presence of substantial amounts of carbon dioxide.

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. In the production of hydrocarbons containing more than two carbon atoms in the molecule or liquid or solid oxygen-containing derivatives of hydrocarbons by conversion of carbon monoxide with hydrogen at an elevated temperature, under a pressure above 5 atmospheres and in the presence of a catalyst, the steps of supplying to the reaction space a mixture of hydrogen, carbon monoxide and inert gas containing less hydrogen than carbon monoxide, the inert gas mainly consisting of carbon dioxide and being in an amount of between 40 and 90 per cent. of the mixture.

2. In the process as claimed in claim 1, employing a gas mixture containing hydrogen and carbon monoxide in the ratio of between less than 50 and 30 parts of hydrogen to between more than 50 and 70 parts of carbon monoxide.

3. The process for the production of hydrocarbons containing more than two carbon atoms in the molecule or liquid or solid oxygen-containing derivatives of hydrocarbons substantially as described in the foregoing Example.

4. Hydrocarbons containing more than two carbon atoms in the molecule or liquid or solid oxygen-containing derivatives of hydrocarbons when prepared by the process particularly described and ascertained.

Dated this 18th day of June, 1937.

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

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