[Second Edition.]

PATENT SPECIFICATION

Application Date: July 13, 1927. No. 18,597/27.

293,572

Complete Left: April 12, 1928.

Complete Accepted: July 12, 1928.

PROVISIONAL SPECIFICATION.

An Improved Process for the Production of Gaseous Hydrocarbons from Gas Mixtures Containing Hydrogen and Oxides of Carbon.

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) to be as follows:—

It is already known that liquid hydrocarbons, or their derivatives may be produced by passing mixtures of oxides of carbon and hydrogen over catalysts, with or without the application of pressure. In some cases, small quantities of gaseous olefines of various kinds are simultaneously formed.

My foreign correspondents have now found that good yields mainly of gaseous olefines, together with other gaseous hydrocarbons may be obtained from gas mixtures containing oxides of carbon and hydrogen, by passing these mixtures over catalysts at a substantially lower velocity than that required for the production of mainly liquid hydrocarbons or their derivatives. For example, when a mixture of carbon monoxide and hydrogen is passed at the rate of 20 litres per hour over 50 cubic centimetres of a suitable contact mass, no gaseous olefines but only liquid products are obtained whereas my foreign correspondents have now found that by passing only one-tenth the amount, namely 2 litres per hour, of the gas mixture over the same quantity of contact mass, gases are obtained with a large content as for example about 10 to 15 per cent. and more of unsaturated gaseous hydrocarbons such as ethylene, propylene and butylene together with ethane and propane, the production of liquid hydrocarbons being practically nil.

According to this method of working the substances chiefly coming under consideration as catalysts comprise metals of the iron group, preferably in conjunction with noble metals or with difficultly reducible oxides, particularly those of the metals belonging to group 6 of the periodic system. The said metallic catalysts may be used by themselves or as alloys, and, if desired, in conjunction with other catalytic or inert substances. Moreover, the apparatus may be lined with the metals or alloys acting as catalysts, or with other metals, or inert materials such as glass, porcelain and the like.

Water gas is a typical example of a gas mixture containing oxides of carbon and hydrogen. The process is carried out with ordinary or elevated pressure and, preferably, at temperatures below red heat that is to say, from about 100° to 400° Centigrade, the gases being kept in circulation if desired.

The olefinic hydrocarbons and ethane may be recovered from the reaction gases by first removing the carbon dioxide with the aid of alkalis, and the like, and subsequently washing the olefines out of the gas mixture, with or without the aid of pressure, either alone by means of sulphuric acid or ammoniacal cuprous chloride solutions or in conjunction with the ethane by means of water or oils. The isolation of the hydrocarbons may also be effected with active charcoal.

The following examples will further illustrate the nature of the said invention which however is not limited thereto.

Example 1.

A gas mixture consisting of 51 per cent. of carbon monoxide, 44 per cent, of hydrogen and 5 per cent. of nitrogen is passed at 370° Centigrade and under a pressure of about 50 atmospheres, at the rate of from 2 to 4 litres per hour with reference to the atmospheric pressure through a high-pressure furnace 15 millimetres in diameter, constructed of a nickel-chromium alloy and containing about 30 cubic centimetres of a contact mass composed of iron and silver. A gas is obtained of the following approximate composition: 60.8 per cent. of CO_2, 13 per cent. of C_nH_{2n}, 12.2 per cent. of

[*Price* 1/-]

C_2H_6, 5.6 per cent, of CH_4. 6 per cent. of N_2, 2.4 per cent, of CO and 0 per cent. of H_2.

EXAMPLE 2.

A gas mixture of the same composition as that in Example 1 is passed, under approximately the same conditions, over a contact mass prepared by fusing iron powder, with the addition of uranyl nitrate, in a current of oxygen. The resulting gas has the following composition: CO_2, 46 per cent.; C_nH_{2n}, 10.2 per cent.; CO, 2.4 per cent.; H_2, 19.8 per cent.; C_2H_6, 2.4 per cent. CH_4, 13.2 per cent.; N_2, 6.0 per cent. After some days working, the activity of the contact mass diminishes owing to the formation of very small quantities of hydrocarbons which volatilise only with great difficulty; but if these be eliminated by roasting the contact mass, or by extraction, the efficacy of the contact mass is restored.

EXAMPLE 3.

Pure, finely divided iron powder is oxidised in a current of oxygen, whereby it melts at white heat. The resulting ferro-ferric oxide is reduced with hydrogen for a period of 10 hours at 460° Centigrade. A gas mixture consisting of 35 per cent. of carbon monoxide, 60 per cent. of hydrogen and 5 per cent. of nitrogen is passed under the conditions described in Example 1 over this contact mass, at 375° Centigrade in a high pressure tube of V2A-steel. The gas-issuing from the contact vessel consists of 27.8 per cent. of CO_2, 6.0 per cent. of C_nH_{2n}. 3.5 per cent. of CO, 28.1 per cent. of H_2, 16.2 per cent, of C_2H_6, 9.6 per cent, of CH_4 and 8.8 per cent. of N_2. Small quantities of hydrocarbons are formed at the same time which may be easily condensed by strongly cooling with solid carbon dioxide, and about half of which boil up to 30° Centigrade. Of this portion about one third consists of olefines.

The small amounts of carbon deposited on the contact mass may be easily burned off, whereupon the contact mass, after having been reduced, again becomes active.

EXAMPLE 4.

A gas containing approximately 35 per cent. of carbon monoxide, 60 per cent. of hydrogen and 5 per cent. of nitrogen is passed under the conditions described in Example 1, at atmospheric pressure and at a temperature of from about 250° to 375° Centigrade over an iron contact mass containing about 1 per cent. of palladium and prepared by joint precipitation from solutions of the respective chlorides or nitrates, followed by reduction in hydrogen at 460° Centigrade. The gas obtained has the following approximate composition: CO_2, 47.4 per cent.; C_nH_{2n}, 4.2 per cent.; CO, 9.0 per cent.; H_2, 22.4 per cent.; C_2H_6, 4.2 per cent.; CH_4, 3.8 per cent.; N_2, 9.0 per cent. At the same time, small quantities of liquid substances may be recovered by strongly cooling.

Dated this 13th day of July, 1927.

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

COMPLETE SPECIFICATION.

An Improved Process for the Production of Gaseous Hydrocarbons from Gas Mixtures Containing Hydrogen and Oxides of Carbon.

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 is already known that liquid hydrocarbons, or their derivatives may be produced by passing mixtures of oxides of carbon and hydrogen over catalysts with or without the application of pressure. In some cases, small quantities of gaseous olefines of various kinds are simultaneously formed.

My foreign correspondents have now found that good yields mainly of gaseous olefines, together with saturated gaseous hydrocarbons may be obtained from gas mixtures containing oxides of carbon and hydrogen, by passing these mixtures over catalysts, comprising iron or cobalt preferably in conjunction with a noble metal or with difficulty reducible oxides of a metal (which expression comprises oxides which are not reduced to metal in a current of hydrogen at temperatures below 600° Centigrade) in particular of a metal belonging to the 6th group of the periodic system, at a substantially lower velocity than that required for the production of mainly liquid hydrocarbons or their derivatives. For example, when a mixture of carbon monoxide and hydrogen is passed at the rate of 20 litres per hour over 50 cubic centimetres of a catalyst containing iron, no gaseous olefines but only liquid products are obtained, whereas my foreign correspondents have now found that by passing only one-tenth the amount, namely 2 litres per hour, of the gas mixture over the same catalyst, gases are obtained with a large content as for example about 10 to 15 per cent. and more of unsaturated gaseous hydrocarbons such as ethylene, propylene and butylene together with ethane and propane, the production of liquid hydrocarbons being practically nil.

The said metallic catalysts may be used by themselves or as alloys, and, if desired, in conjunction with other catalytic or inert substances. Moreover, the apparatus may be lined with the metals or alloys acting as catalysts, or with other metals or inert materials such as glass, porcelain and the like.

Water gas is a typical example of a gas mixture containing oxides of carbon and hydrogen. The process is carried out at ordinary or elevated pressure and, preferably, at temperatures below red heat that is to say, from about 100° to 400° Centigrade the gases being kept in circulation if desired.

The olefinic hydrocarbons and ethane may be recovered from the reaction gases by first removing the carbon dioxide with the aid of alkalis, and the like, and subsequently washing the olefines out of the gas mixture, with or without the aid of pressure, either alone by means of sulphuric acid or ammoniacal cuprous chloride solutions or in conjunction with the ethane by means of water or oils. The isolation of the hydrocarbons may also be effected with active charcoal.

The following examples will further illustrate how the said invention may be carried out in practice but the invention is not limited thereto.

EXAMPLE 1.

A gas mixture consisting of 51 per cent. of carbon monoxide, 44 per cent. of hydrogen and 5 per cent. of nitrogen is passed at 370° Centigrade and under a pressure of about 50 atmospheres, at the rate of from 2 to 4 litres per hour with reference to the atmospheric pressure and normal temperature, through a high-pressure furnace 15 millimetres in diameter, constructed of a nickel-chromium alloy and containing about 30 cubic centimetres of a catalyst composed of iron and silver. A gas is obtained of the following approximate composition: 60.8 per cent. of CO_2, 13 per cent. of C_nH_{2n}, 12.2 per cent. of C_2H_6, 5.6 per cent. of CH_4, 6 per cent. of N_2, 2.4 per cent. of CO and 0 per cent. of H_2.

EXAMPLE 2.

A gas mixture of the same composition as that in Example 1 is passed, under approximately the same conditions, over a contact mass prepared by fusing iron powder, with the addition of uranyl nitrate, in a current of oxygen. The resulting gas has the following composition: CO_2, 46 per cent.; C_nH_{2n}, 10.2 per cent.; CO, 2.4 per cent.; H_2, 19.8 per cent.; C_2H_6, 2.4 per cent.; CH_4, 13.2 per cent.; N_2, 6.0 per cent. After some days working, the activity of the catalyst diminishes owing to the formation of very small quantities of hydrocarbons which volatilise only with great difficulty; but if these be eliminated by roasting the catalyst, or by extraction, the efficacy of the catalyst is restored.

EXAMPLE 3.

Pure, finely divided iron powder is oxidised in a current of oxygen, whereby it melts at white heat. The resulting, ferro-ferric oxide is reduced with hydrogen for a period of 10 hours at 460° Centigrade. A gas mixture consisting of 35 per cent. of carbon monoxide, 60 per cent. of hydrogen and 5 per cent. of nitrogen is passed under the conditions described in Example 1 over this contact mass, at 375° Centigrade in a high pressure tube of V2A-steel. The gas issuing from the catalyst vessel consists of 27.8 per cent. of CO_2, 6.0 per cent. of C_nH_{2n}, 3.5 per cent. of CO, 28.1 per cent. of H_2, 16.2 per cent. of C_2H_6, 9.6 per cent. of CH_4 and 8.8 per cent. of N_2. Small quantities of hydrocarbons are formed at the same time which may be easily condensed by strongly cooling with solid carbon dioxide, and about half of which boil up to 30° Centigrade. Of this portion about one third consists of olefines.

The small amounts of carbon deposited on the contact mass may be easily burned off, whereupon the catalyst, after having been reduced, again becomes active.

EXAMPLE 4.

A gas containing approximately 35 per cent. of carbon monoxide, 60 per cent. of hydrogen and 5 per cent. of nitrogen is passed under the conditions described in Example 1, at atmospheric pressure and at a temperature of from about 250° to 375° Centigrade over an iron catalyst containing about 1 per cent, of palladium and prepared by joint precipitation from solutions of the respective chlorides or nitrates, followed by reduction in hydrogen at 460° Centigrade. The gas obtained has the following approximate composition: CO_2, 47.4 per cent.; C_nH_{2n}, 4.2 per cent.; CO, 9.0 per cent.; H_2, 22.4 per cent.; C_2H_6, 4.2 per cent.; CH_4, 3.8 per cent.; N_2, 9.0 per cent. At the same time, small quantities of liquid substances may be recovered by strongly cooling.

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 gaseous olefines together with saturated gaseous hydrocarbons which consists in passing a gas mixture containing an oxide of carbon and hydrogen, preferably under elevated pressure, at elevated temperatures over a catalyst comprising at least one of the metals iron and cobalt at a substantially lower velocity than that required for the production of mainly liquid hydrocarbons or derivatives thereof.

2. A modification of the process in accordance with the preceding claiming clause which consists in passing the gas mixture over a catalyst as defined in Claim 1 which further contains a noble metal, or a difficultly reducible oxide, or other catalytically acting or inert material or mixtures of the said materials,

3. The production of gaseous olefines together with saturated gaseous hydrocarbons substantially as described in each of the foregoing examples.

4. Gaseous olefines and saturated gaseous hydrocarbons when prepared in accordance with the preceding claiming clauses.

Dated this 12th day of April, 1928.
JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London, W.C. 2,
Agents.

Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 56A.—125/12/1928].