PATENT SPECIFICATION

Application Date: April 3, 1936. No. 9888/36.

464,308

Complete Specification Left: May 21, 1936.

Complete Specification Accepted: April 15, 1937.

PROVISIONAL SPECIFICATION

Improvements in the Production of Hydrocarbons

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 carrying out exothermic gas reactions, in particular those with carbonaceous gases, such as the conversion of carbon monoxide by means of hydrogen into liquid, solid and/or gaseous hydrocarbons or their derivatives, it may happen that products of high molecular weight formed during the reaction settle on the catalyst and impair its activity. Such reactions are frequently accompanied by a strong evolution of heat which may readily lead to thermal congestion in the catalysts, whereby it is difficult or quite impossible without the use of special measures to maintain the desired reaction temperature. Thus for example in the synthesis of hydrocarbons from carbon monoxide and hydrogen, substances of high molecular weight in particular paraffin waxes, are formed which cover the catalyst and cause a decrease in the catalytic efficiency. Moreover the said reaction proceeds with very great evolution of heat which necessitates a great subdivision of the reaction chamber in order to lead away the heat.

My foreign correspondents have now found that in the said reactions, working free from trouble can be obtained and in particular the activity of the catalyst does not subside by trickling the catalyst during the reaction with a liquid medium while avoiding the formation of a liquid surface in the reaction chamber. By this trickling, the settling of products of high molecular weight on the catalyst is prevented because any products of high molecular weight deposited on the catalyst are dissolved off again and furthermore a cooling of the catalyst takes place so that it is possible to arrange the catalyst in tubes of any width. Since the liquid medium trickles down at the surface of the catalyst and covers the latter only in a thin layer, the gases to be brought into reaction can readily contact with the catalyst because the distance which the gases have to travel through the liquid is only very small. This is of considerable advantage as compared with working while wholly or partially filling the reaction chamber with liquid in which case the gases cannot contact so readily with the catalyst.

The liquid medium used according to this invention may be passed in the same direction as the gases or in countercurrent thereto. As suitable media, those liquids in which the products of high molecular weight formed during the reaction are readily dissolved or suspended are especially suitable, in particular organic solvents, such as middle oils, heavy oils, paraffin oils and anthracene oils, and in particular liquid substances formed during the reaction itself, i.e. the characteristic oil. Of this characteristic oil, it is preferable to use fractions of which at least a considerable portion remains liquid under the reaction conditions. Similarly when using foreign liquids, at least a part of the same should remain liquid under the reaction conditions. The amount of liquid medium is preferably selected so that there is always a thin layer of liquid present on the surface of the catalyst. In some cases it may be advantageous temporarily to interrupt the trickling, especially when a temporary increase in temperature at the catalyst is desired.

It has also been found to be advantageous to withdraw the liquid medium together with the reaction products from the reaction chamber at the lower end thereof. A separation of the liquid medium from the reaction products may be effected by known methods, as for example by strong cooling, distillation or the use of selective solvents.

The liquid medium is preferably led in a cycle over the catalyst, the liquid and high molecular reaction products absorbed by the liquid medium being removed therefrom continuously or at certain intervals of time.

The reaction of carbon monoxide with hydrogen to form hydrocarbons according to this invention may be carried out at any desired pressures. For example a slight excess pressure, such as 2, 3, 5 or 10 atmospheres, or higher pressures, such as 50, 100 atmospheres or more, may be used. Atmospheric pressure or reduced pressure may also be employed.

The reactions are carried out at the usual temperatures, the reaction of carbon monoxide with hydrogen to form hydrocarbons being carried out preferably above 150° Centigrade and advantageously between 200° and 450° Centigrade.

The composition of the initial gases may be as usual.

The following Example, given with respect to the accompanying drawing which illustrates an example of apparatus suitable according to this invention, will further illustrate the nature of this invention but the invention is not restricted to this Example, or to the particular example of apparatus shewn.

EXAMPLE.

A mixture of carbon monoxide and hydrogen is led through a pipe 2 into the upper part of a reaction chamber 1 charged with a rigidly arranged catalyst consisting for example of iron with 5 per cent. of aluminium oxide. Paraffin oil is introduced through the pipe 3, the liquid being distributed uniformly over the cross-section of the catalyst space by the nozzle 4. The catalyst, which is arranged in the reaction chamber in the form of pieces, is thus uniformly trickled by the paraffin oil. No liquid level is maintained in the catalyst chamber so that the spaces between the pieces of catalyst are almost entirely filled by the reaction gases. The mixture of paraffin oil and liquid and gaseous reaction products flow downwards into a cooled separating vessel 5 in which the separation of the liquid from gases takes place and in which a liquid level 8 is maintained. The gaseous portion, consisting mainly of unconverted initial gas, is withdrawn through the pipe 6 and may be further reacted in a second reaction chamber or returned to the same reaction chamber for further reaction. The liquid portion is removed through the pipe 7.

Dated this 3rd day of April, 1936.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

COMPLETE SPECIFICATION

Improvements in the Production of Hydrocarbons

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 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 conversion of carbon monoxide by means of hydrogen into liquid solid and/or gaseous hydrocarbons it may happen that products of high molecular weight, in particular paraffin waxes formed during the reaction settle on the catalyst and impair its activity. The strong evolution of heat occurring in this reaction readily leads to thermal congestion in the catalysts, whereby it is difficult or quite impossible without the use of special measures to maintain the desired reaction temperature such as a great subdivision of the reaction chamber in order to lead away the heat.

My foreign correspondents have now found that the said conversion of carbon monoxide and hydrogen into hydrocarbons which is very sensitive as regards the temperature to be maintained can be carried out very smoothly without great trouble or difficulties as regards apparatus by continuously or periodically trickling the rigidly arranged catalyst with a liquid during the conversion whereby the catalyst is maintained at a desired temperature. When working in this manner the activity of the catalyst does not subside during the reaction. Since the reaction is to be carried out in the gas phase the formation of a liquid level in the reaction chamber should be avoided. By the said trickling the settling of products of high molecular weight on the catalyst is prevented because any products of high molecular weight deposited on the catalyst may be dissolved off again and furthermore a cooling of the catalyst takes place so that it is possible to arrange the catalyst in tubes of any width. Since the liquid medium trickles down at the surface of the catalyst and covers the latter only in a thin layer, the gases to be brought into reaction can readily contact with the catalyst because the distance which the gases have to travel through the liquid is only very small. This is of considerable advantage as compared with working while wholly or partly filling the reaction chamber with liquid in which case the gases cannot contact so readily with the catalyst.

As catalysts suitable for the said conversion may be mentioned any substances catalytically promoting this conversion which are rigidly arranged either in the form of pieces or precipitated on carriers, advantageously metallic carriers. Thus pieces, rings, balls or nets of catalytic substances, for example those containing metals of the iron group, such as iron or nickel, may be employed. Precipitates of catalytic substances on pumice stone or pieces, nets or balls of metal, clay, porcelain or glass may also be used.

The liquid medium used according to this invention may be passed in the same direction as the gases or in countercurrent thereto. Suitable liquids are alcohols, hydrocarbons and other liquids which do not injure the catalysts and which remain liquid under the working conditions or are only partly vaporised during the cooling process. As liquids suitable for the reduction of carbon monoxide are especially those in which the products of high molecular weight formed during the reaction are readily dissolved or suspended, in particular organic solvents, such as middle oils, heavy oils, paraffin oils and anthracene oils, and in particular liquid substances formed during the reaction itself, i.e. the characteristic oil. Of this characteristic oil, it is preferable to use fractions of which at least a considerable portion remains liquid under the reaction conditions. Similarly when using foreign liquids, at least a part of the same should remain liquid under the reaction conditions. The amount of liquid medium is preferably selected so that there is always a thin layer of liquid present on the surface of the catalyst. In some cases it may be advantageous temporarily to interrupt the trickling, especially when a temporary increase in temperature at the catalyst is desired. The liquid is advantageously pumped in circulation, if desired while interposing heat-exchangers. The operation according to the present invention may be effected at any desired pressures. For example a slight excess pressure, such as 2, 3, 5 or 10 atmospheres, or higher pressures, such as 50, 100 atmospheres or more, may be used. Atmospheric pressure or reduced pressure may also be employed.

It has also been found to be advantageous to withdraw the liquid medium together with the reaction products from the reaction chamber at the lower end thereof. A separation of the liquid medium from the reaction products may be effected by known methods, as for example by strong cooling, distillation or the use of selective solvents.

When passing the liquid medium in a cycle over the catalyst the liquid and high molecular reaction products absorbed by the liquid medium may be removed therefrom continuously or at certain intervals of time.

The conversion is carried out at the usual temperature preferably above 150° Centigrade and advantageously between 200° and 450° Centigrade.

The composition of the initial gases may be as usual.

The following Example which is given with respect to the drawing accompanying the Provisional specification which drawing illustrates an example of apparatus suitable according to this invention, will further illustrate how this invention may be carried out in practice but the the invention is not restricted to this Example or to the particular example of apparatus shewn.

EXAMPLE.

A mixture of carbon monoxide and hydrogen is led through a pipe 2 into the upper part of a reaction chamber 1 charged with a rigidly arranged catalyst consisting for example of iron with 5 per cent. of aluminium oxide. Paraffin oil is introduced through the pipe 3, the liquid being distributed uniformly over the cross-section of the catalyst space by the nozzle 4. The catalyst, which is arranged in the reaction chamber in the form of pieces, is thus uniformly trickled by the paraffin oil. No liquid level is maintained in the catalyst chamber so that the spaces between the pieces of catalyst are almost entirely filled by the reaction gases. The mixture of paraffin oil and liquid and gaseous reaction products flows downwards into a cooled separating vessel 5 in which the separation of the liquid from gases takes place and in which a liquid level 8 is maintained. The gaseous portion, consisting mainly of unconverted initial gas, is withdrawn through the pipe 6 and may be further reacted in a second reaction chamber or return to the same reaction chamber for further reaction. The liquid portion is removed through the pipe 7.

We are aware that it has already been proposed to produce liquid hydrocarbons and oxygen derivatives of hydrocarbons by treating carbonaceous liquids or gases with hydrogen in the presence of an added medium which remains liquid and does not take part in the reaction under the reaction conditions. According to this proposal, either the conversion takes place entirely in the liquid phase or the liquid medium is added in such manner as to cause the formation of a liquid level in the reaction space.

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 carrying out the conversion of carbon monoxide with hydrogen for the production of liquid, solid and/or gaseous hydrocarbons, in the presence of rigidly arranged catalysts which comprises trickling liquid media over these catalysts during the conversion while avoiding the formation of a liquid level in the reaction space.

2. In the process as claimed in claim 1, employing liquid media in which the reaction products formed are readily dissolved.

3. In the process as claimed in claim 1 or 2, in which there are formed by the conversion higher boiling liquid substances remaining liquid under the conditions of working employing such liquid substances as media to be trickled over the catalysts.

4. The process for carrying out exothermic catalytic hydrogenation reactions substantially as described in the foregoing Example.

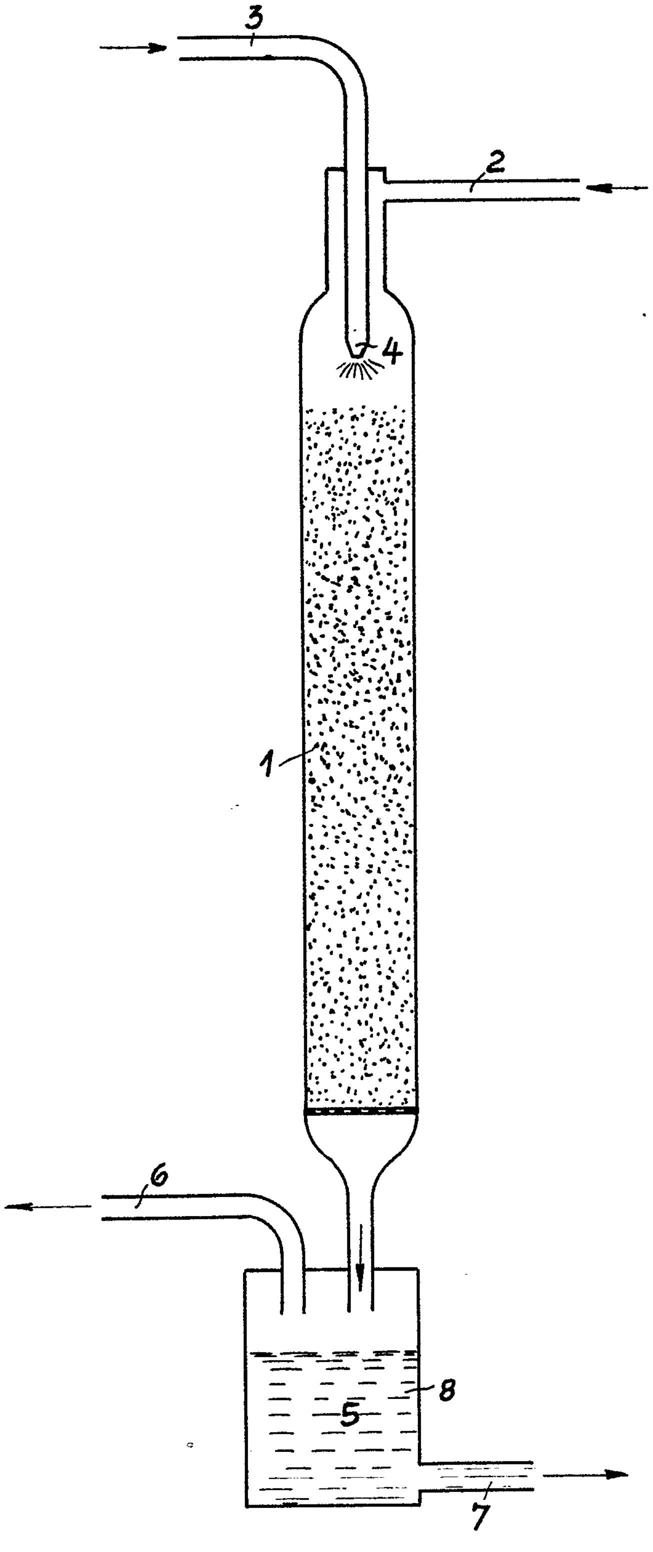
5. Liquid, solid and gaseous hydrocarbons, when obtained by the process particularly described and ascertained.

6. Apparatus for carrying out the conversion of carbon monoxide and hydrogen into liquid solid or gaseous hydrocarbons substantially as herein described and shewn in the drawing accompanying the Provisional specification.

Dated this 21st day of May, 1936.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1937.

[This Drawing is a reproduction of the Original on a reduced scale.]



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