PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Process for the Conversion of Carbon Monoxide with Hydrogen into Hydrocarbons

I, HAROLD EDWIN POTTS, Chartered Patent Agent, of 12, Church Street, Liverpool, in the County of Lancaster, Subject of the King of Great Britain, do hereby declare the nature of this invention which has been communicated to me by N. V. Internationale Koolwaterstoffen Synthese Maatschappij (International Hydrocarbon Synthesis Company), of 20, Wassenaarscheweg, The Hague, Holland, a Dutch Company, to be as follows:—

In the conversion of carbon monoxide with hydrogen into hydrocarbons with more than one carbon atom in the molecule after a shorter or longer period of time a decrease in the activity of the catalysts used usually occurs, which primarily is caused by the precipitation of substances of high molecular weight on the catalysts. It has already been proposed to reactivate the catalysts by removing these substances of high molecular weight by an extraction with solvents or by a treatment with hydrogen or steam at elevated temperatures. When working in this way the conversion has, however, to be discontinued, which owing to the necessity of carrying out the reactivation repeatedly, involves a considerable decrease in production.

Unless otherwise stated the parts herein referred to are by volume.

My foreign correspondents have now found that the said decrease in the activity of the catalysts can be avoided if the conversion of carbon monoxide with hydrogen into hydrocarbons with more than one carbon atom in the molecule is carried out by employing a gas mixture containing about two parts or less of hydrogen to one part of carbon monoxide (synthesis proper) and alternately, at intervals, a gas mixture richer in hydrogen containing at least 2.5 parts of hydrogen to one part of carbon monoxide, thereby reactivating the catalyst. The reactivated catalyst may be even more active than the original catalyst.

The said gas mixture richer in hydrogen alternately passed over the catalyst advantageously contains about 2.5 to 10 parts of hydrogen to one part of carbon monoxide. With such a mixture the catalyst is in continuous industrial operation repeatedly restored to about its original activity in a short time, whilst a considerable conversion into hydrocarbons of the desired kind takes place simultaneously, so that no very considerable decrease in production occurs during reactivation.

The synthesis proper may, for example, be carried out with a gas, which contains 30 per cent. of carbon monoxide and 60 per cent. of hydrogen and, when the activity of the catalyst has decreased below a certain degree, the catalyst may be reactivated with a gas containing 15 per cent. of carbon monoxide and 75 per cent. of hydrogen or with 12 per cent. of carbon monoxide and 80 per cent. of hydrogen (remainder inert gases).

The process in accordance with the present invention can be carried out with particular advantage by working in two or more reaction vessels and alternately introducing into each of them synthesis gas rich in carbon monoxide and a gas rich in hydrogen as hereinbefore defined, the catalyst being reactivated with the latter. When working in this way, the switching over may also already be carried out, when the decrease in catalyst activity has not yet become definitely noticeable, and in this case the mixture richer in hydrogen need be passed through the reaction vessel only for a short time to restore the catalyst activity. Therefore the single working periods with the alternate gas mixtures may be taken within wide limits as convenient. This method of working makes an uninterrupted production and employment of the synthesis gas and of the said gas rich in hydrogen possible.

The catalysts the activity of which has been decreased owing to the precipitation thereon of substances of high molecular weight, may also be treated with a solvent for a short time and thereafter the gas rich in hydrogen as hereinbefore defined may be passed over them. This measure is recommended, when the activity of the catalyst has been strongly

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decreased. After long intervals of time one of the usual regeneration methods may also be applied.

The synthesis proper may be carried out under any suitable pressure, for example, ordinary or elevated pressure. Thus, pressures of 5, 20, 50, 100, 200 or more atmospheres may be employed. The temperatures are also the usual ones and are as a rule between 170° and 370° Centigrade. The reactivation is preferably carried out under the same conditions as to pressure and temperature. The process may be carried out in one or more stages and in the latter case the same or different conditions, for example, the same or different pressures or catalysts, may be employed in the individual stages.

The process may be carried out with any catalysts suitable therefor, for example, fused ferrosoferric oxide with suitable additions (particularly substances containing silicon and/or titanium) or sintered iron catalysts or mixtures of cobalt with activating substances, such as, for example, thorium oxide, suitably on carriers, such as, for example, kieselguhr, or catalysts containing nickel or mixtures of the said catalysts.

The process of the present invention allows of prolonging the lifetime of the catalysts to a multiple of that previously obtainable without a substantial decrease in the production of hydrocarbons occurring due to interruption of the desired synthesis.

Apart from this the process has the advantage that the gas mixtures containing about two parts or less of hydrogen to one part of carbon monoxide employed therein for the synthesis proper are initial materials which are particularly readily available, because the content of carbon monoxide in many gas mixtures produced industrially or industrially available is very considerable. To produce a synthesis gas of the desired composition in many cases a portion of this carbon monoxide must be converted with steam to hydrogen and carbon dioxide, the latter being then, if desired, removed. It is desirable, since thereby valuable carbon monoxide is converted to carbon dioxide, to keep the proportion of carbon monoxide to be converted with steam as low as possible.

The synthesis gases for the present process may be produced in any suitable manner, in particular by gasification of solid fuels, such as coke, bituminous coal, brown coal or of fuels of lesser value or by conversion of natural or refinery gases with steam and carbon dioxide or by an incomplete combustion, of natural gases.

The said gas mixture richer in hydrogen may be produced in any suitable manner, for example, by one or more conversions of other gases carried out to give the desired composition, or by mixing two or more gases in the proportions, which yield the desired composition, for example, by mixing a gas consisting completely or almost completely of hydrogen, for example electrolytically produced hydrogen, with carbon monoxide, which may also contain a certain amount of hydrogen, for example, synthesis gas. The production by mixing can take place by branching off a part of the synthesis gas shortly before that vessel in which the reactivation of the catalyst is just being carried out, and adding hydrogen in a proportion sufficient for the reactivation to the said branched off portion. The production by conversion of other gases can be carried out by a catalytic treatment of a part of the synthesis gas with steam or by a cracking of the residual gases of the synthesis, which contain hydrocarbons.

Finally the said gas rich in hydrogen can be obtained by a partial conversion of the carbon monoxide in a portion of the synthesis gas with steam into carbon dioxide and hydrogen, followed by a conversion of the residual carbon monoxide into methane after removal of the carbon dioxide formed or by a separation by means of cooling to low temperatures, diffusion and the like of a fraction rich in hydrogen from the residual gas issuing from the synthesis.

The following Example will further illustrate the nature of the said invention but it should be understood that the invention is not limited to the Example.

EXAMPLE.

Over a cobalt catalyst containing 18 per cent. of thorium oxide a gas is passed at 180° Centigrade and under ordinary pressure, which contains carbon monoxide and hydrogen in the proportion of 1:2. After 28 days the activity of the catalyst has so far diminished that only about 50 cubic centimetres of liquid hydrocarbons per cubic metre of the carbon monoxide-hydrogen mixture is formed in contrast to a maximum production of 85 cubic centimetres. Hereupon the catalyst is treated for two days with a gas, which contains carbon monoxide and hydrogen in the proportion of 1:4, whereby a production of liquid products of about 70 per cent. of that first obtained in the synthesis proper is obtained. After reverting to the gas first introduced the catalyst at once produces about 95 cubic centimetres of liquid hydrocarbons

per cubic metre of the carbon monoxide-hydrogen mixture.

Dated this 16th day of March, 1939.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

COMPLETE SPECIFICATION

Process for the Conversion of Carbon Monoxide with Hydrogen into Hydrocarbons

I, HAROLD EDWIN POTTS, Chartered Patent Agent, of 12, Church Street, Liverpool, in the County of Lancaster, Subject of the King of Great Britain, do hereby declare the nature of this invention which has been communicated to me by N. V. Internationale Koolwaterstoffen Synthese Maatschappij (International Hydrocarbon Synthesis Company), of 20, Wassenaarscheweg, The Hague, Holland, a Dutch Company, 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 with hydrogen into hydrocarbons with more than one carbon atom in the molecule after a shorter or longer period of time a decrease in the activity of the catalysts used usually occurs, which primarily is caused by the precipitation of substances of high molecular weight on the catalysts. It has already been proposed to reactivate the catalysts by removing these substances of high molecular weight by an extraction with solvents or by a treatment with hydrogen or steam at elevated temperatures. When working in this way the conversion has, however, to be discontinued, which owing to the necessity of carrying out the reactivation repeatedly, involves a considerable decrease in production.

Unless otherwise stated the parts herein referred to are by volume.

My foreign correspondents have now found that the said decrease in the activity of the catalysts can be avoided if the conversion of carbon monoxide with hydrogen into hydrocarbons with more than one carbon atom in the molecule is carried out by employing a gas mixture containing about two parts or less of hydrogen to one part of carbon monoxide (synthesis proper) and alternately, at intervals, a gas mixture richer in hydrogen containing at least 2.5 parts of hydrogen to one part of carbon monoxide, thereby reactivating the catalyst. The reactivated catalyst may be even more active than the original catalyst.

The said gas mixture richer in hydrogen alternately passed over the catalyst advantageously contains about 2.5 to 10 parts of hydrogen to one part of carbon monoxide. With such a mixture the catalyst is in continuous industrial operation repeatedly restored to about its original activity in a short time, whilst a considerable conversion into hydrocarbons of the desired kind takes place simultaneously, so that no very considerable decrease in production occurs during reactivation.

The synthesis proper may, for example, be carried out with a gas, which contains 30 per cent. of carbon monoxide and 60 per cent. of hydrogen and, when the activity of the catalyst has decreased below a certain degree, the catalyst may be reactivated with a gas containing 15 per cent. of carbon monoxide and 75 per cent. of hydrogen or with 12 per cent. of carbon monoxide and 80 per cent. of hydrogen (remainder inert gases).

The process in accordance with the present invention can be carried out with particular advantage by working in two or more reaction vessels and alternately introducing into each of them synthesis gas rich in carbon monoxide and a gas rich in hydrogen as hereinbefore defined, the catalyst being reactivated with the latter. When working in this way, the switching over may also be carried out, when the decrease in catalyst activity has not yet become definitely noticeable, and in this case the mixture richer in hydrogen need be passed through the reaction vessel only for a short time to restore the catalyst activity. Therefore the single working periods with the alternate gas mixtures may be taken within wide limits as convenient. This method of working makes an uninterrupted production and employment of the synthesis gas and of the said gas rich in hydrogen possible.

The catalysts the activity of which has been decreased owing to the precipitation thereon of substances of high molecular weight, may also be treated with a solvent for a short time and thereafter the gas rich in hydrogen as hereinbefore defined may be passed over them. This measure is recommended, when the activity of the catalyst has been strongly decreased. After long intervals of time one of the usual regeneration methods may also be supplied.

The synthesis proper may be carried

out under any suitable pressure, for example, ordinary or elevated pressure. Thus, pressures of 5, 20, 50, 100, 200 or more atmospheres may be employed. The temperatures are also the usual ones and are as a rule between 170° and 370° Centigrade. The reactivation is preferably carried out under the same conditions as to pressure and temperature. The process may be carried out in one or more stages and in the latter case the same or different conditions, for example, the same or different pressures or catalysts, may be employed in the individual stages.

The process may be carried out with any known catalysts, for example, fused ferrosoferric oxide with suitable additions (particularly substances containing silicon and/or titanium) or sintered iron catalysts or mixtures of cobalt with activating substances, such as, for example, thorium oxide, suitably on carriers, such as, for example, kieselguhr, or catalysts containing nickel or mixtures of the said catalysts.

The process of the present invention allows of prolonging the lifetime of the catalysts to a multiple of that previously obtainable without a substantial decrease in the production of hydrocarbons occurring due to interruption of the desired synthesis.

Apart from this the process has the advantage that the gas mixtures containing about two parts or less of hydrogen to one part of carbon monoxide employed therein for the synthesis proper are initial materials which are particularly readily available, because the content of carbon monoxide in many gas mixtures produced industrially or industrially available is very considerable. To produce a synthesis gas of the desired composition in many cases a portion of this carbon monoxide must be converted with steam to hydrogen and carbon dioxide, the latter being then, if desired, removed. It is desirable, since thereby valuable carbon monoxide is converted to carbon dioxide, to keep the proportion of carbon monoxide to be converted with steam as low as possible.

The synthesis gases for the present process may be produced in any suitable manner, in particular by gasification of solid fuels, such as coke, bituminous coal, brown coal or of fuels of lesser value or by conversion of natural or refinery gases with steam and carbon dioxide or by an incomplete combustion, of natural gases.

The said gas mixture richer in hydrogen may be produced in any suitable manner, for example, by one or more conversions of other gases carried out to give the desired composition, or by mixing two or more gases in the proportions, which yield the desired composition, for example, by mixing a gas consisting completely or almost completely of hydrogen, for example electrolytically produced hydrogen, with carbon monoxide, which may also contain a certain amount of hydrogen, for example, synthesis gas. The production by mixing can take place by branching off a part of the synthesis gas shortly before that vessel in which the reactivation of the catalyst is just being carried out, and adding hydrogen in a proportion sufficient for the reactivation to the said branched off portion. The production by conversion of other gases can be carried out by a catalytic treatment of a part of the synthesis gas with steam or by a cracking of the residual gases of the synthesis, which contain hydrocarbons.

Finally the said gas rich in hydrogen can be obtained by a partial conversion of the carbon monoxide in a portion of the synthesis gas with steam into carbon dioxide and hydrogen, followed by a conversion of the residual carbon monoxide into methane after removal of the carbon dioxide formed or by a separation by means of cooling to low temperatures, diffusion and the like of a fraction rich in hydrogen from the residual gas issuing from the synthesis.

The following Example will further illustrate the nature of the said invention and how the same is to be carried out in practice, but it should be understood that the invention is not limited to the Example.

EXAMPLE.

Over a cobalt catalyst containing 18 per cent. of thorium oxide a gas is passed at 180° Centigrade and under ordinary pressure, which contains carbon monoxide and hydrogen in the volume proportion of 1:2. After 28 days the activity of the catalyst has so far diminished that only about 50 cubic centimetres of liquid hydrocarbons per cubic metre of the carbon monoxide-hydrogen mixture is formed in contrast to a maximum production of 85 cubic centimetres. Hereupon the catalyst is treated for two days with a gas, which contains carbon monoxide and hydrogen in the volume proportion of 1:4, whereby a production of liquid products of about 70 per cent. of that first obtained in the synthesis proper is obtained. After reverting to the gas first introduced the catalyst at once produces about 95 cubic centimetres of liquid hydrocarbons per cubic metre of the carbon monoxide-hydrogen mixture.

Having now particularly described and

ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. In the manufacture and production of hydrocarbons with more than one carbon atom in the molecule by conversion of carbon monoxide with hydrogen, the improvement which comprises converting a gas mixture containing about two parts or less of hydrogen to one part of carbon monoxide (synthesis proper) and alternately, at intervals, a gas mixture richer in hydrogen containing at least 2.5 parts of hydrogen to one part of carbon monoxide, thereby reactivating the catalyst.

2. A process as claimed in claim 1, which comprises employing a gas mixture richer in hydrogen containing from 2.5 to 10 parts of hydrogen to one part of carbon monoxide.

3. A process as claimed in claim 1 or 2, which comprises converting a gas mixture containing 60 per cent. of hydrogen and 30 per cent. of carbon monoxide and alternately, at intervals, a gas mixture containing 75 per cent. of hydrogen and 15 per cent. of carbon monoxide the remainder being inert gases.

4. A process as claimed in claim 1 or 2, which comprises converting a gas mixture containing 60 per cent. of hydrogen and 30 per cent. of carbon monoxide and alternately, at intervals, a gas mixture containing 80 per cent. of hydrogen and 12 per cent. of carbon monoxide the remainder being inert gases.

5. A process as claimed in any of claims 1 to 4, which comprises converting simultaneously each of the said two gas mixtures in a separate reaction vessel or set of vessels and, at intervals, interchanging the said gas mixtures.

6. A process as claimed in any of claims 1 to 4, which comprises converting the gas mixture richer in hydrogen in the presence of a catalyst previously treated with a solvent for the removal of high boiling reaction products from the said catalyst.

7. A process as claimed in any of claims 1 to 6, which comprises adding hydrogen or a gas consisting substantially of hydrogen, to a part of the gas mixture for the synthesis proper to produce the gas mixture richer in hydrogen.

8. A process as claimed in any of claims 1 to 7, which comprises converting the gas mixture richer in hydrogen under the same conditions as to temperature and pressure as in the synthesis proper.

9. A process for the manufacture and production of hydrocarbons with more than one carbon atom in the molecule, substantially as described in the foregoing Example.

10. Hydrocarbons with more than one carbon atom in the molecule when obtained by the process claimed in any of the preceding claiming clauses.

Dated this 10th day of January, 1940.

W. P. THOMPSON & CO.,
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Chartered Patent Agents.

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