RESERVE COPY

PATENT SPECIFICATION

Application Date: March 11, 1939. No. 7909/39.

Complete Specification Left: Jan. 11, 1940.

Complete Specification Accepted: Sept. 26, 1940.

526,814

2713

PROVISIONAL SPECIFICATION

Process for the Synthesis of Hydrocarbons from Mixtures of Carbon Monoxide and Hydrogen

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:—

It is already known that the synthesis gases which are employed for the production of hydrocarbons with more than one carbon atom in the molecule, in particular liquid or fusible hydrocarbons from carbon monoxide and hydrogen must be purified very thoroughly to remove catalyst poisons. Even a very small sulphur content causes a rapid decrease in the activity of the catalysts. In the case of some synthesis gases, especially those which are obtained by gasification with a gasifying agent of carbonaceous solid materials more recent than bituminous coal, for example, brown coals, the activity of the catalyst is already decreased from the beginning of the reaction, and these difficulties occur even when the said gases have been carefully purified from compounds.

These latter difficulties in the synthesis therefore appear to be due to noxious impurities other than sulphur compounds present in such gases, such as gum formers, which impair the catalyst activity.

My foreign correspondents have now found that the said decrease in catalyst activity can be avoided in the synthesis of hydrocarbons with more than one carbon atom in the molecule, especially liquid hydrocarbons, from carbon monoxide and hydrogen, if a synthesis gas consisting of a mixture of carbon monoxide and hydrogen contingently together with other gases, is converted, which after its production has been heated at high temperatures, above 800° Centigrade, preferably at least 1000° Centigrade, and simultaneously or thereafter has been freed from the hydrocarbon sulphide, which may have been contained in the same in the form of organic sulphur compounds and/or as such.

The best results are attained by heating at temperatures within the range of 1000° to about 1250°, say at 1100° or 1200° Centigrade. Higher temperatures than about 1400° Centigrade are usually not required or desired but may be employed where convenient.

By the said heating the organic sulphur compounds which may be present in the gases are practically completely converted into hydrogen sulphide, which can then easily be removed in a known manner.

Beside the sulphur compounds also the aforesaid other noxious constituents are decomposed at the high temperatures applied in the present process.

The surprising effect with the process of the present invention is particularly striking when employing synthesis gases obtained by gasification with gasifying agents of solid carbonaceous materials, more recent than bituminous coal, more particularly brown coal, since when heated according to the process of the present invention the said gases are equal to the most suitable synthesis gases obtained from coke from bituminous coal and are even occasionally superior to them. However, the process is valuable for synthesis gases obtained from other carbonaceous materials, such as bituminous coal, coke and the like, if these give rise to the aforesaid difficulties. Also other gases, suitable for the synthesis of hydrocarbons may sometimes advantageously be treated according to the process of the present invention, for example those obtained from neutral or refinery gases by conversion with steam and, if desired, carbon dioxide.

The gases employed in the process of the present invention may contain higher or smaller amounts of accompanying gases which do not disturb or may even be desired for the synthesis, for example, carbon dioxide or methane.

Advantageously, the heating of the gases according to the present process is carried out in the heat accumulators or heat-exchangers provided with filling material or in a combination of these two apparatus, so that a part of the added amount of heat is retained and only the heat to maintain the requisite high temperature must be newly supplied. The so-called cowpers are very suitable apparatus for heating the gases according to the present process. The high temperature may be attained in any desired manner, for example, by means of direct heating, which may be carried out by supplying oxygen (this heating method is especially suitable for bringing the hot material to the requisite high temperature) or by means of gas burners, electrical heating rods, etc. In many cases it is advantageous to preheat the gas indirectly and to supply oxygen to the preheated material to bring it to the requisite high temperature. It is also possible to heat the gases by passing them over periodically heated heat regenerating masses.

The heated synthesis gases may be cooled by direct or indirect cooling to the temperatures suitable for conversion in the synthesis into hydrocarbons, for example, by means of heat exchange with fresh synthesis gas to be heated for purification, or by injecting water free from oxygen or by utilising their heat for distilling the synthesis product or for the production of steam.

Advantageously heat exchangers which are constructed of metals withstanding corrosion by sulphur and chemical attack by the reaction gases are used. In case the initial gases contain much organic sulphur, it is occasionally advantageous to use as filling material in the heat accumulator, or, as the case may be heat exchanger, burnt lime, burnt dolomite, bauxite or like materials, which accelerate the conversion of the organic sulphur compounds into hydrogen sulphide.

In order to obtain good results in the synthesis of hydrocarbons, the synthesis gases preferably contain carbon monoxide and hydrogen in certain definite proportions, dependent on the particular reaction conditions adopted and the products which it is desired to obtain, for example a proportion of carbon monoxide to hydrogen of between about 2:1 to 1:3, say 1:1.2 to 1:2. The proportion of carbon monoxide to hydrogen in the synthesis gases may, if necessary, be brought within the desired range after the purification according to the process of the present invention, by conversion of a portion of the carbon monoxide with steam to hydrogen and carbon dioxide, and, if desired, removing the latter, and/or by mixing the synthesis gases with hydrogen or gases containing hydrogen and carbon monoxide in other proportions.

The synthesis of hydrocarbons with the gases purified according to the process of the present invention, can be carried out under the conditions usual for this reaction, for example, at temperatures between 175° and 220° Centigrade and under ordinary or elevated presure, in the presence of catalysts. The catalysts may be washed with an oil continuously or at intervals, in which latter case the synthesis may be continued or interrupted. In the case of interruption of the synthesis, conditions different from those during the synthesis proper may be employed, for example, lower temperatures and higher pressures, especially temperatures up to 50° Centigrade and high pressures up to 150 atmospheres or more.

The synthesis may be carried out in the liquid or in the gaseous phase.

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

EXAMPLE 1.

Water gas which has been obtained by gasification of brown coal and which contains per cubic metre about 100 milligrams of organic sulphur, is passed at 1200° Centigrade over bauxite, thereupon freed from the hydrogen sulphide formed by means of a mass absorbing hydrogen sulphide and after cooling passed over a cobalt-thorium oxide catalyst at ordinary pressure and at about 180° Centigrade. The average yield of liquid hydrocarbons produced in one passage amounts to about 115 cubic centimetres per cubic metre of carbon monoxide-hydrogen mixture in contrast to only about 90 cubic centimetres per cubic metre of the gas when using the same initial gas after purification from organically bound sulphur in the usual manner with alkalised iron oxide mass at about 300° Centigrade. The "half-value-time" of the catalyst (i.e. the time in which the catalyst activity decreases to half its original activity when the reaction has been started with preheated gas, so that the yield of liquid hydrocarbons is decreased to half the original value) was about 20 per cent longer than with the gas which had been purified in the usual manner.

EXAMPLE 2.

A carbon monoxide-hydrogen mixture obtained from brown coal briquettes by gasification with oxygen is passed at 1100° Centigrade over fragments of quartz and is used for the hydrocarbon synthesis after removal of the hydrogen sulphide formed by means of gas purifying mass. The gas which is passed on to the synthesis is completely free from sulphur and an average yield of liquid hydrocarbons is obtained which is 25 cubic centimetres per cubic metre of the gas higher than in a synthesis which for purposes of comparison has been carried out at the same time and in the same furnace (the furnace contains two separate catalyst tubes in the same block of aluminium), in which synthesis a part of the same initial gas was used, which had been purified from organically bound sulphur in the usual manner.

In case a carbon monoxide-hydrogen mixture obtained from coke or bituminous coal is purified in the usual manner and then subjected to synthesis under the same conditions, a yield of liquid hydrocarbons is obtained which is 8 to 10 cubic centimetres per cubic metre of the gas lower than with the same gas mixture which has been heated to 1100° Centigrade as described in the preceding paragraph.

Dated this 10th day of March, 1939.
W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

COMPLETE SPECIFICATION

Process for the Synthesis of Hydrocarbons from Mixtures of Carbon Monoxide and Hydrogen

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:—

It is already known that the synthesis gases which are employed for the production of hydrocarbons with more than one carbon atom in the molecule, in particular liquid or wax-like hydrocarbons from carbon monoxide and hydrogen must be purified very thoroughly to remove catalyst poisons. Even a very small sulphur content causes a rapid decrease in the activity of the catalysts. In the case of some synthesis gases, especially those which are obtained by gasification with a gasifying agent of carbonaceous solid materials more recent than bituminous coal, for example, brown coals, the activity of the catalyst is already decreased from the beginning of the reaction, and these difficulties occur even when the said gases have been carefully purified from sulphur compounds.

These latter difficulties in the synthesis therefore appear to be due to noxious impurities other than sulphur compounds present in such gases, such as gum formers, which impair the catalyst activity.

My foreign correspondents have now found that the said decrease in catalyst activity can be avoided in the synthesis of hydrocarbons with more than one carbon atom in the molecule, especially liquid hydrocarbons, from carbon monoxide and hydrogen, if a synthesis gas consisting of a mixture of carbon monoxide and hydrogen if desired together with other gases, is converted, which after its production has been heated at high temperatures of at least 1000° Centigrade, and thereafter has been freed from the hydrogen sulphide, which has been contained in the same as such and/or which has been formed from organic sulphur compounds occurring in the said mixture.

The best results are attained by heating at temperatures within the range of 1000° to about 1250°, say at 1100° or 1200° Centigrade. Higher temperatures than about 1400° Centigrade are usually not required or desired but may be employed where convenient.

The duration of sojourn in the heating zone giving the best results can be readily determined by one skilled in the art and may lie within wide limits. As a rule the best results are obtained if the gases are heated in the hot zone for about 0.5 to 1 second. A rate of flow of for example, about 0.9 cubic metres per second per cubic metre of reaction space may be maintained.

By the said heating the organic sulphur compounds which may be present in the gases are practically completely converted into hydrogen sulphide, which can then easily be removed in a known manner.

Beside the sulphur compounds also the aforesaid other noxious constituents are decomposed at the high temperatures applied in the present process.

The surprising effect with the process of the present invention is particularly striking when employing synthesis gases obtained by gasification with gasifying agents of solid carbonaceous materials, more recent than bituminous coal, more particularly brown coal, since when heated according to the process of the present invention the said gases are equal to the most suitable synthesis gases obtained from coke from bituminous coal and are even occasionally superior to them. However, the process is valuable for synthesis gases obtained from other carbonaceous materials, such as bituminous coal, coke and the like, if these give rise to the aforesaid difficulties. Also other gases, suitable for the synthesis of hydrocarbons may sometimes advantageously be treated according to the process of the present invention, for example, those obtained from natural or refinery gases by conversion with steam and, if desired, carbon dioxide.

The gases employed in the process of the present invention may contain higher or smaller amounts of accompanying gases which do not disturb or may even be desired for the synthesis, for example, carbon dioxide or methane.

Advantageously, the heating of the gases according to the present process is carried out in the heat accumulators or heat exchangers provided with filling material or in a combination of these two apparatus, so that a part of the added amount of heat is retained and only the heat to maintain the requisite high temperature must be newly supplied. The so-called cowpers are very suitable apparatus for heating the gases according to the present process. The high temperature may be attained in any desired manner, for example, by means of direct heating, which may be carried out by supplying oxygen (this heating method is especially suitable for bringing the hot material to the requisite high temperature) or by means of gas burners, electrical heating rods, etc. In many cases it is advantageous to preheat the gas indirectly and to supply oxygen in stages or gradually to the preheated material so that by regulated combustion it is brought to the requisite high temperature, and kept at this temperature for the requisite time. It is also possible to heat the gases by passing them over periodically heated heat regenerating masses.

The heated synthesis gases may be cooled by direct or indirect cooling to the temperatures suitable for conversion in the synthesis into hydrocarbons, for example, by means of heat exchange with fresh synthesis gas to be heated for purification, or by injecting water free from oxygen or by utilizing their heat for distilling the synthesis product or for the production of steam.

Advantageously heat exchangers which are constructed of metals withstanding corrosion by sulphur and chemical attack by the reaction gases are used. In case the initial gases contain much organic sulphur, it is occasionally advantageous to use as filling material in the heat accumulator, or, as the case may be heat exchanger, burnt lime, burnt dolomite, or bauxite, which accelerate the conversion of the organic sulphur compounds into hydrogen sulphide.

In order to obtain good results in the synthesis of hydrocarbons, the synthesis gases preferably contain carbon monoxide and hydrogen in certain definite proportions, dependent on the particular reactions, dependent on the particular reaction conditions adopted and the products which it is desired to obtain, for example a proportion of carbon monoxide to hydrogen of between about 2:1 to 1:3, say 1:1.2 to 1:2. The proportion of carbon monoxide to hydrogen in the synthesis gases, may, if necessary, be brought within the desired range after the purification according to the process of the present invention, by conversion of a portion of the carbon monoxide with steam to hydrogen and carbon dioxide, and, if desired, removing the latter, and/or by mixing the synthesis gases with hydrogen or gases containing hydrogen and carbon monoxide in other proportions.

The synthesis of hydrocarbons with the gases purified according to the process of the present invention, can be carried out under the conditions usual for this reaction, for example, at temperatures between 175° and 220° Centigrade and under ordinary or elevated pressure, in the presence of catalysts. The catalysts may be washed with an oil continuously or at intervals, in which latter case the synthesis may be continued or interrupted. If the synthesis is interrupted for this purpose conditions different from those during the synthesis proper may be employed during such period of interruption, for example, lower temperatures and higher pressures, especially temperatures up to 50° Centigrade and high pressures up to 150 atmospheres or more.

The synthesis may be carried out in the liquid phase, i.e. in presence of liquid hydrocarbons or in the gaseous phase.

The following Examples will further illustrate how the invention may be carried out in practice, but it should be understood that the invention is not limited to the said Examples.

EXAMPLE 1.

Water gas which has been obtained by gasification of brown coal and which contains per cubic metre about 100 milligrams of organic sulphur, is passed at 1200° Centigrade over bauxite in such a way that the gas remains 0.5 second in the hot zone. Thereupon the gas is freed from the hydrogen sulphide formed by means of a mass absorbing hydrogen sulphide e.g. an iron oxide purification mass, and after cooling passed over a cobalt-thorium oxide catalyst at ordinary pressure and at about 180° Centigrade. The average yield of liquid hydrocarbons produced in one passage amounts to about 115 cubic centimetres per cubic metre of carbon monoxide-hydrogen mixture in contrast to only about 90 cubic centimetres per cubic metre of the gas when using the same initial gas after purification from organically bound sulphur in the usual manner with alkalised iron oxide mass at about 300° Centigrade. The "half-value-time" of the catalyst (i.e. the time in which the catalyst activity decreases to half its original activity when the reaction has been started with preheated gas, so that the yield of liquid hydrocarbons is decreased to half the original value) was about 20 per cent longer than with the gas which had been purified in the usual manner.

EXAMPLE 2.

A carbon monoxide-hydrogen mixture obtained from brown coal briquettes by gasification with oxygen is passed at 1100° Centigrade over fragments of quartz in such a way that the gas remains 3/4 second in the hot zone and is used for the hydrocarbon synthesis after removal of the hydrogen sulphide formed by means of an iron oxide purifying mass. The gas which is passed on to the synthesis is completely free from sulphur and an average yield of liquid hydrocarbons is obtained which is 25 cubic centimetres per cubic metre of the gas higher than in a synthesis which for purposes of comparison has been carried out at the same time and in the same furnace (the furnace contains two separate catalyst tubes in the same block of aluminium), in which synthesis a part of the same initial gas was used, which had been purified from organically bound sulphur in the usual manner.

In case a carbon monoxide-hydrogen mixture obtained from coke or bituminous coal is purified in the usual manner and then subjected to synthesis under the same conditions, a yield of liquid hydrocarbons is obtained which is 8 to 10 cubic centimetres per cubic metre of the gas lower than with the same gas mixture which has been heated to 1100° Centigrade as described in the preceding paragraph.

We are aware that it has been previously proposed in specification No. 14200/09 to purify illuminating gas after removal of sulphuretted hydrogen therefrom, but which still contains carbon bisulphide, by reheating the gas to a high temperature with or without the addition of steam whereby the carbon bisulphide is converted into sulphuretted hydrogen, and then the sulphuretted hydrogen removed.

A temperature of between 400° C. and 1000° C. may be employed in this process, but in practice a temperature between 400° C. and 900° C. is preferred.

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. A process for the synthesis of hydrocarbons with more than one carbon atom in the molecule, especially liquid hydrocarbons, from carbon monoxide and hydrogen, which comprises converting a synthesis gas consisting of a mixture of carbon monoxide and hydrogen, if desired together with other gases, which after its production has been heated at high temperatures of at least 1000° Centigrade, and thereafter has been freed from the hydrogen sulphide which has been contained in the same as such and/or which has been formed from organic sulphur compounds occurring in the said mixture.

2. A process as claimed in Claim 1, which comprises heating the synthesis gas at a temperature within the range of 1000° to about 1250° Centigrade.

3. A process as claimed in any of Claims 1 or 2, which comprises heating the gases in the hot zone during about 0.5 to 1 second.

4. A process as claimed in any of Claims 1 to 3, which comprises converting a synthesis gas obtained by gasification with a gasifying agent of solid carbonaceous materials more recent than bituminous coal, such as brown coal.

5. A process as claimed in any of Claims 1 to 3, which comprises converting in the synthesis a synthesis gas obtained from natural or refinery gases by conversion with steam and, if desired, carbon dioxide.

6. A process as claimed in any of Claims 1 to 5, in which the heating is carried out in heat accumulators or heat exchangers, provided with filling material, or in a combination of these two apparatus.

7. A process as claimed in any of Claims 1 to 6, in which the heating is carried out in cowpers.

8. A process as claimed in Claim 6 or 7, which comprises using as filling material burnt lime, burnt dolomite, or bauxite.

9. A process for the synthesis of hydrocarbons with more than one carbon atom in the molecule, especially liquid hydro-

carbons, substantially as described in the foregoing Examples.

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

Dated this 10th day of January, 1940.

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

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1940.