PATENT SPECIFICATION

Application Date: Jan. 4, 1937. No. 251/37.

480,820

Complete Specification Left: Oct. 18, 1937.

Complete Specification Accepted: March 1, 1938.

3659

PROVISIONAL SPECIFICATION

Improvements in or relating to the Production of Hydrogen-containing Gases

We, THE NATIONAL COKE & OIL COMPANY LIMITED, a British Company, and JOHN LLOYD STREVENS, a British Subject, both of 82, King William Street, London, E.C.4, do hereby declare the nature of this invention to be as follows:—

This invention is for improvements in or relating to the production of hydrogen-containing gases and has particular reference to the production of gaseous mixtures containing hydrogen and carbon-monoxide which are to be used in the preparation of aliphatic hydrocarbons. This conversion of mixtures of hydrogen and carbon-monoxide to hydrocarbons may be carried out, inter alia by passing the mixture over a catalyst consisting of one or more metals of the 8th group of the periodic classification.

It has been found that in order to secure a high percentage conversion of the gaseous mixture into hydrocarbons, it is desirable that the volume of hydrogen in the gaseous mixture should be about twice the volume of the carbon-monoxide, and it is an object of the present invention to provide a process in which the ratio of hydrogen and carbon-monoxide is substantially of this order. It is a further object of the invention to employ in the production of such gaseous mixtures permanent gas, and, it may be, solid residues formed in processes for the distillation of carbonaceous material as described in one or other of British Specifications Nos: 393,602; 421,556; 426,645; 427,960; 429,757; 435,187; 437,730 or 447,328.

It has been found that water gas, coke oven gas and the like contain carbon-monoxide and hydrogen in the proportions of from 4:5 by volume in the case of water gas to 7:48 in the case of coke oven gas and are therefore unsuitable for use directly in the synthesis of hydrocarbons. Similarly, the permanent gas resulting from the distillation processes described in the above-mentioned British Patent Specifications normally contains only small proportions of carbon-monoxide and relatively large amounts of hydrogen, the proportion of hydrogen to carbon-monoxide amounting in one example to 36:5 by volume.

According to the present invention, there is provided a process for the production of a gaseous mixture suitable for use in the catalytic manufacture of hydrocarbons, and particularly aliphatic hydrocarbons, which process consists in the preparation of a mixture of water gas and permanent gas formed in one or other of the distillation processes above referred to, so that the mixture contains hydrogen and carbon-monoxide in the ratio of about 2:1 by volume.

It has been found that the other gases present in the gaseous mixture, e.g. carbon-dioxide, saturated hydrocarbons such as methane, unsaturated hydrocarbons such as ethylene, and inert gases, such as nitrogen, have comparatively little effect upon the catalytic reaction, and act merely as diluents.

The water gas may be prepared by any one of the usual methods from coals, cokes or like carbonaceous materials, and in one modification of the invention, it may be produced by the employment of the solid residue (in the briquetted or the unbriquetted form) derived from the distillation processes described in the above-mentioned specifications. In this form of the invention, the processes described in the above-mentioned specifications provide all the raw materials necessary for the catalytic synthesis of hydrocarbons.

Before the gaseous mixture is employed for the synthesis of hydrocarbons, it must be freed from sulphur-compounds, including hydrogen sulphide and organic sulphur compounds. This purification may conveniently take place after the mixing of the water gas and permanent gas, the hydrogen-sulphide being removed, e.g. by passing the gases over iron-oxide and the organic sulphur compounds being removed, e.g. by a catalytic process.

In a modification of the present invention, the content of hydrogen in the mixed gas may be increased by treating water gas with steam by the

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known process in order to convert it to carbon-dioxide and hydrogen and removing the carbon-dioxide either by scrubbing with aqueous alkali or with water under pressure. The gas thus obtained is rich in hydrogen and may be introduced into the gaseous mixture.

When briquetted carbonaceous material is employed for the production of the water gas, these briquettes may be made, e.g. in accordance with the process described in Specification No: 13871/36 (Serial No. 472,340).

Following is a description by way of example of one method of carrying the invention into effect.

Water gas is prepared by passing air and steam alternately over red-hot carbonaceous residue produced by the process described in one or other of the specifications hereinbefore referred to, this type of carbonaceous material being particularly reactive in the water gas manufacturing process. The water gas contains about 50% hydrogen, 40% carbon-monoxide and small amounts of carbon-dioxide, methane and nitrogen. There is blended with the water gas permanent gas produced by the process described in the above-mentioned specifications, this gas containing approximately 36% hydrogen, 5% carbon-monoxide, 39% methane and smaller proportions of carbon-dioxide, nitrogen and unsaturated hydrocarbons. The gas is mixed in such proportions that the mixture contains two volumes of hydrogen to one of carbon-monoxide and in addition some 30—35% of hydrocarbons, nitrogen and carbon-dioxide, which have little effect other than as a diluent on the catalytic reaction.

The mixed gases are passed through an iron-oxide purifier to remove hydrogen-sulphide and are treated for the removal of organic sulphur compounds by a known catalytic process. The gaseous mixture is then subjected directly to treatment with a catalyst, preferably at relatively low temperature and pressure, for the formation of hydrocarbons therefrom. The gaseous products leaving the catalyst vessel are passed through a condenser and the permanent gases may, if desired, be returned again to the gas stream entering the catalyst chamber.

Dated this 4th day of January, 1937.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden,
London, E.C.1,
Chartered Patent Agents.

COMPLETE SPECIFICATION

Improvements in or relating to the Production of Hydrogen-containing Gases

We, THE NATIONAL COKE & OIL COMPANY LIMITED, a British Company, and JOHN LLOYD STEEVENS, a British Subject, both of 32, King William Street, London, E.C.4, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention is for improvements in or relating to the production of hydrogen-containing gases and has particular reference to the production of gaseous mixtures containing hydrogen and carbon-monoxide which are to be used in the preparation of aliphatic hydrocarbons. This conversion of mixtures of hydrogen and carbon-monoxide to hydrocarbons may be carried out, inter alia, by passing the mixture over a catalyst consisting of one or more metals of the 8th group of the periodic classification.

It has been found that in order to secure a high percentage conversion of the gaseous mixture into hydrocarbons it is desirable that the volume of hydrogen in the gaseous mixture should be about twice the volume of the carbon-monoxide, and it is an object of the present invention to provide a process in which the ratio of hydrogen and carbon-monoxide is brought substantially to this order. It is a further object of the invention to employ in the production of such gaseous mixtures permanent gas, and, it may be, solid residues formed in processes for the distillation of carbonaceous material as described in one or other of British Patent Specifications Nos. 393,602; 421,556; 426,645; 427,960; 429,757; 435,187; 437,730 or 447,328. A process of the kind described in any of the above mentioned specifications is hereinafter referred to as a process of the type described.

It has been found that certain gases including water gas and coke oven gas contain carbon-monoxide and hydrogen in the proportions of from 4 to 5 by

volume in the case of water gas and 7 to 48 in the case of coke oven gas and are therefore unsuitable for use directly in the synthesis of hydrocarbons. Similarly, the permanent gas resulting from the distillation processes described in the above mentioned British Patent Specifications normally contains only small proportions of carbon-monoxide and relatively large amounts of hydrogen, the proportion of hydrogen to carbon-monoxide amounting in one example to 36 to 5 by volume.

According to the present invention, there is provided a process for the production of a gaseous mixture suitable for use in the catalytic manufacture of hydrocarbons, and particularly of aliphatic hydrocarbons, which process consists in blending with water gas or with coke oven gas containing carbon-monoxide and hydrogen in proportions ranging between 4 to 5 and 7 to 48 by volume such a proportion of permanent gas produced in a process of the type described for the distillation of carbonaceous material that the resulting gaseous mixture contains hydrogen and carbon-monoxide substantially in the proportion of 2 to 1 by volume.

It has been found that the other gases present in the gaseous mixture, e.g. carbon-dioxide, saturated hydrocarbons such as methane, unsaturated hydrocarbons such as ethylene, and inert gases, such as nitrogen, have comparatively little effect upon the catalytic reaction, and act merely a diluents.

The water gas may be prepared by any one of the usual methods from coals, cokes or like carbonaceous materials, and in one modification of the invention, it may be produced by the employment of the solid residue (in the briquetted or the unbriquetted form) derived from a distillation process of the type described. In this form of the invention, one or other of the processes described in the above mentioned specifications provide all the raw materials necessary for the catalytic synthesis of hydrocarbons.

Before the gaseous mixture is employed for the synthesis of hydrocarbons, it must be freed from sulphur compounds, including hydrogen sulphide and organic sulphur compounds. This purification may conveniently take place after the mixing of the water gas and permanent gas, the hydrogen-sulphide being removed, e.g. by passing the gases over iron-oxide and the organic sulphur compounds being removed, e.g. by a catalytic process.

In a modification of the present invention, the content of hydrogen in the mixed gas may be increased by treating water gas with steam by the known process in order to convert it to carbon-dioxide and hydrogen and removing the carbon-dioxide either by scrubbing with aqueous alkali or with water under pressure. The gas thus obtained is rich in hydrogen and may be introduced into the gaseous mixture.

When briquetted carbonaceous material is employed for the production of the water gas, these briquettes may be made, e.g. in accordance with the process described in Specification No. 13871/36 (Serial No. 472,340).

Following is a description by way of example of one method of carrying the invention into effect.

EXAMPLE.

Water gas is prepared by passing air and steam alternately over red-hot carbonaceous residue (which may be in the form of briquettes) produced by the process described in one or other of the specifications hereinbefore referred to, this type of carbonaceous material being particularly reactive in the water gas manufacturing process. The water gas contains about 50% hydrogen, 40% carbon-monoxide and small amounts of carbon-dioxide, methane and nitrogen. There is blended with the water gas permanent gas produced by the process described in the above-mentioned specifications, this gas containing approximately 36% hydrogen, 5% carbon-monoxide, 39% methane and smaller proportions of carbon-dioxide, nitrogen and unsaturated hydrocarbons. The gas is mixed in such proportions that the mixture contains two volumes of hydrogen to one of carbon-monoxide and in addition some 30—35% of hydrocarbons, nitrogen and carbon-dioxide, which have little effect other than as a diluent on the catalytic reaction.

The mixed gases are passed through an iron-oxide purifier to remove hydrogen-sulphide and are treated for the removal of organic sulphur compounds by a known catalytic process. The gaseous mixture is then subjected directly to treatment with a catalyst, preferably at relatively low temperature and pressure, for the formation of hydrocarbons therefrom. The gaseous products leaving the catalyst vessel are passed through a condenser and the permanent gases may, if desired, be returned again to the gas stream entering the catalyst chamber.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to

be performed, we declare that what we claim is:—

1. A process for the production of a gaseous mixture suitable for use in the catalytic manufacture of hydrocarbons, and particularly of aliphatic hydrocarbons, which process consists in blending with water gas or with coke oven gas containing carbon-monoxide and hydrogen in proportions ranging between 4 to 5 and 7 to 48 by volume such a proportion of permanent gas produced in a process of the type described for the distillation of carbonaceous material that the resulting gaseous mixture contains hydrogen and carbon-monoxide substantially in the proportion of 2 to 1 by volume.

2. A process as claimed in claim 1, wherein the water gas is prepared from carbonaceous residue produced in a process of the type described for the distillation of a mixture of solid carbonaceous material and oil.

3. A process as claimed in claim 2 wherein the solid carbonaceous residue is employed in the form of briquettes.

4. A process as claimed in any one of the preceding claims wherein prior to employing the gaseous mixture for the manufacture of hydrocarbons the mixture of water gas and permanent gas is treated for the removal of hydrogen-sulphide therefrom.

5. A process as claimed in any one of the preceding claims wherein the content of hydrogen in the mixed gases is increased by treating water gas with steam to form carbon-dioxide and hydrogen and thereafter removing the carbon-dioxide.

6. A process for the production of a gaseous mixture suitable for use in the catalytic manufacture of hydrocarbons substantially as described in the specific example hereinbefore set forth.

7. A gaseous mixture containing hydrogen and carbon-monoxide substantially in the ratio of 2 to 1 by volume whenever prepared or produced by the process hereinbefore particularly described and ascertained.

Dated this 18th day of October, 1937.
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Chartered Patent Agents.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1938.