PATENT SPECIFICATION

Application Date: Oct. 13, 1937. No. 27884/37.

503,622

Complete Specification Left: Sept. 28, 1938.

Complete Specification Accepted: April 12, 1939.

PROVISIONAL SPECIFICATION

A Process for the Manufacture and Production of a Product Rich in Unsaturated Hydrocarbons from Carbon Monoxide and Hydrogen

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 of Germany) to be as follows:—

In the reaction of carbon monoxide with hydrogen at atmospheric or only moderately increased pressures of for example 5, 10 or 20 atmospheres, there are usually formed mainly saturated hydrocarbons which knock strongly when used as benzines in motors. In order to increase the amount of unsaturated hydrocarbons in the reaction product and thus to improve the non-knocking properties of the benzine, it has already been proposed to carry out the reaction with less hydrogen than is necessary for complete reaction of the carbon monoxide. In many cases, however the activity of the catalyst then subsides very soon for example by deposition of carbon, and moreover there is the danger that a part of the carbon monoxide may be unconverted.

My foreign correspondents have now found that a product rich in unsaturated hydrocarbons can be obtained in a simple manner by using for the catalytic reaction in the gas phase at atmospheric or slightly increased pressures, gas mixtures which contain less than 2 parts by volume of hydrogen for each part by volume of carbon monoxide and adding further hydrogen in the course of the reaction.

It is advantageous to work by starting from a gas containing between 0.9 and 1.5 parts by volume of hydrogen for each part by volume of carbon monoxide and maintaining this ratio during the reaction by the addition of further hydrogen. It is preferable to use in all at least such an amount of hydrogen that there are 2 parts by volume of hydrogen for each part by volume of carbon monoxide and that the reaction proceeds according to the equation:—

$$nCO + 2nH_2 = (CH_2)_n + nH_2O.$$

For carrying out the said process there may be mentioned as suitable catalysts in particular cobalt or nickel on carriers, if desired together with other substances, or mixtures of iron and copper, sintered metals of the iron group, metals of the iron group with manganese and copper or with aluminium or with substances withdrawing water, such as thorium oxide, or iron which has been obtained by the reduction of ferrosoferric oxide, if desired with the addition of silicic acid, titanium oxide or alumina.

The procedure may, for example, be as follows:—

A mixture of carbon monoxide and hydrogen containing between 0.9 and 1.5 parts by volume of hydrogen for each part by volume of carbon monoxide is led at atmospheric pressure and at a temperature of from 160° to 350° Centigrade over a catalyst of the said kind. At a plurality of places in the reaction chamber hydrogen is led in in the cold or preheated state in such manner that at every part of the reaction chamber practically the aforesaid ratio of hydrogen to carbon monoxide is maintained. In all, such an amount of hydrogen is used that there are about 2 parts by volume of hydrogen for each part by volume of carbon monoxide.

As a rule it is necessary, especially when working at atmospheric pressure, to use gases which are free from sulphur and sulphur compounds. It is also advantageous that there should be present only small amounts of inert constituents, such as carbon dioxide or nitrogen. For example there may be used as initial gas a watergas which has been desulphurised and which contains 45 per cent. of carbon monoxide and 51 per cent. of hydrogen and during the course of the reaction there may be added hydrogen which has been prepared from the same watergas by reaction of the carbon monoxide with steam and washing out the carbon dioxide formed.

The following Example will further illustrate the nature of this invention but the invention is not restricted to this Example.

[*Price* 1/-]

EXAMPLE.

A watergas freed from sulphur compounds which contains 42.7 per cent. of carbon monoxide, 49.1 per cent. of hydrogen and the remainder nitrogen and carbon dioxide is led at 195° Centigrade at atmospheric pressure over a catalyst of cobalt, thorium and sodium applied to kieselguhr. In the reaction, which leads to the formation of benzine and hydrocarbons of higher boiling point, carbon monoxide and hydrogen are used up in the ratio 1:2 so that the gas becomes poorer in hydrogen. There is therefore added at four places in the reaction chamber about equal portions of a gas free from sulphur compounds and consisting to the extent of 95 per cent. of hydrogen the amount added being in all 36 litres for each 100 litres of watergas. For each cubic metre of the gas used in all, there are obtained 112 grams of liquid product by condensation and absorption from the gases leaving the reaction vessel. The benzine obtainable therefrom by distillation up to 180° Centigrade has an octane value of 55.

By working under otherwise identical conditions but by adding the whole of the hydrogen at the start, about the same yield of liquid products is obtained, but the benzine has an octane value of only 47.

Dated this 13th day of October, 1937.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields,
London, W.C.2,
Agents.

COMPLETE SPECIFICATION

A Process for the Manufacture and Production of a Product Rich in Unsaturated Hydrocarbons from Carbon Monoxide and Hydrogen

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) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

By reaction of carbon monoxide with hydrogen at atmospheric or only moderately increased pressures of for example 5, 10 or 20 atmospheres, there are usually formed mainly saturated hydrocarbons which knock strongly when used as motor fuel. In order to increase the amount of unsaturated hydrocarbons in the reaction product and thus to improve the non-knocking properties of the benzine produced, it has been proposed to carry out the reaction with less hydrogen than is necessary for a complete reaction of the carbon monoxide. In many cases, however, the activity of the catalyst then subsides very soon, for example by deposition of carbon, and moreover there is the drawback that a part of the carbon monoxide may be left unconverted.

It has already been proposed in respect of British Specification No. 454,948 to increase the amount of unsaturated hydrocarbons in the reaction product by subjecting mixtures of carbon monoxide and hydrogen, which contain not less hydrogen than carbon monoxide, first to a partial conversion and then after completely or partially removing the condensable reaction products subjecting the unconverted reaction gas to a further conversion after gas capable of reacting, for example hydrogen, has been added.

My foreign correspondents have now found that a product rich in unsaturated hydrocarbons can be obtained in a simple manner by using for the catalytic reaction in the gas phase at atmospheric or slightly increased pressures, gas mixtures which contain less than 2 parts by volume of hydrogen for each part by volume of carbon monoxide, passing the total amount of reaction participants and products through the whole reaction space and adding further hydrogen in the course of the reaction.

It is advantageous to start with a gas containing between 0.9 and 1.5 parts by volume of hydrogen for each part by volume of carbon monoxide and to maintain this ratio during the reaction by adding further hydrogen. It is preferable to use in all at least such an amount of hydrogen that there are about 2 parts by volume of hydrogen for each part by volume of carbon monoxide and that the reaction proceeds according to the equation:—

$$nCO + 2nH_2 = (CH_2)_n + nH_2O.$$

As suitable catalysts for carrying out the said process there may be mentioned in particular cobalt or nickel on carriers, if desired together with other substances, or mixtures of iron and copper, sintered metals of the iron group, metals of the iron group with manganese and copper or with aluminium or with substances, such as thorium oxide, having a dehydrating action or iron which has been obtained by the reduction of ferrosoferric oxide, if desired with an addition of silicic acid, titanium oxide or alumina.

The procedure may, for example, be as follows:—

A mixture of carbon monoxide and hydrogen containing between 0.9 and 1.5 parts by volume of hydrogen for each part by volume of carbon monoxide is led at atmospheric pressure and at a temperature of from 160° to 350° Centigrade over a catalyst of the said kind. At a plurality of places in the reaction chamber hydrogen is led in in a cold or preheated state in such manner that at every part of the reaction chamber practically the aforesaid ratio of hydrogen to carbon monoxide is maintained. In all, about 2 parts by volume of hydrogen for each part by volume of carbon monoxide are used.

As a rule it is necessary, especially when working at atmospheric pressure, to use gases which are free from sulphur and sulphur compounds. It is also advantageous that there should be present only small amounts of inert constituents, such as carbon dioxide or nitrogen. For example there may be used as initial gas a watergas which has been desulphurised and which contains 45 per cent. of carbon monoxide and 51 per cent. of hydrogen, and during the course of the reaction there may be added hydrogen which has been prepared from the same watergas by decomposition of the carbon monoxide with steam and washing out the carbon dioxide formed.

The content of olefines in the final products depends upon the conditions employed, in particular on the nature of the catalyst and on the temperature. The lower boiling fractions of the said products of the nature of benzine usually contain more than 20 per cent. and more particularly between 50 and 80 per cent. of olefines.

The following Example will further illustrate how the said invention may be carried out in practice but the invention is not restricted to this Example.

EXAMPLE.

A watergas freed from sulphur compounds which contains 42.7 per cent. of carbon monoxide, 49.1 per cent. of hydrogen and as the remainder nitrogen and carbon dioxide is led at 195° Centigrade at atmospheric pressure over a catalyst composed of cobalt and the oxides of thorium and sodium applied to kieselguhr. In the reaction, which leads to the formation of benzine and hydrocarbons of higher boiling point, carbon monoxide and hydrogen are used up in the ratio 1:2 so that the gas becomes poorer in hydrogen. There is therefore added at four subsequent places in the reaction chamber in about equal portions a gas free from sulphur compounds consisting to the extent of 95 per cent. of hydrogen the amount added being in all 36 litres for each 100 litres of watergas. For each cubic metre of gas used in all, there are obtained 112 grams of liquid product by condensation and absorption from the gases leaving the reaction vessel. The benzine fraction thereof distilling up to 180° Centigrade has the octane number 55.

When working under otherwise identical conditions but adding the whole of the hydrogen at the start, about the same yield of liquid products is obtained, but the benzine fraction has an octane number of only 47.

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 catalytic conversion of carbon monoxide and hydrogen at atmospheric or slightly increased pressures into hydrocarbon products rich in unsaturated hydrocarbons which comprises reacting a gas which contains less than 2 parts by volume of hydrogen for each part by volume of carbon monoxide, passing the total amount of reaction participants and products through the whole reaction space and adding further hydrogen to the gas in the ocurse of the reaction.

2. In the process as claimed in claim 1, starting from a gas containing between 0.9 and 1.5 parts by volume of hydrogen for each part by volume of carbon monoxide and maintaining this ratio during the reaction by the addition of further hydrogen.

3. In the process as claimed in claim 1 or 2, adding in the course of the reaction so much further hydrogen that the total amount by volume of hydrogen is about twice the amount of carbon monoxide employed.

4. The process for the production of hydrocarbon products rich in unsaturated hydrocarbons by the reaction of carbon monoxide with hydro-

gen substantially as described in the foregoing Example.

5. Hydrocarbon products rich in unsaturated compounds when obtained by the process particularly described and ascertained.

Dated this 28th day of September, 1938.

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.—1939