PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Hydrocarbons or their Derivatives from Carbon Monoxide and Hydrogen.

We, I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT, of Frankfort - on - Main, Germany, a Joint Stock Company organized under the Laws of Germany, 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 :—

The specification No. 468,434, which is of prior date but which is not a prior publication, describes a process for the manufacture and production of hydrocarbons or their oxygen - containing derivatives from carbon monoxide and hydrogen according to which the reaction of the said gases is carried out at elevated temperatures and while using catalysts in a liquid medium which consists of the oils obtained by the reaction of an amount of the same initial material having previously been treated under the same or similar conditions and which contains considerable amounts of constituents which are gaseous or vapours under the temperature and pressure conditions used, i.e. which boil below the reaction temperature at the pressure used. The said liquid medium is hereinafter referred to for the sake of brevity as the proper oil. Suitable initial gas mixtures mentioned in the said specification are those containing from 10 to 80 per cent. of carbon monoxide and from 90 to 20 per cent. of hydrogen, preferably those containing 30 to 70 per cent. of carbon monoxide and 70 to 30 per cent. of hydrogen. In the specific Examples given in the said specification, the initial gas used contains 40 per cent. of carbon monoxide and 60 per cent. of hydrogen by volume, or 47 per cent. of carbon monoxide and 53 per cent. of hydrogen.

We have now found that the said reaction in the said proper oil proceeds especially advantageously by using as the initial gas mixture one containing from 45 to 30 parts by volume of hydrogen to 55 to 70 parts by volume of carbon monoxide. With these ratios of the reactants in the initial gas the undesirable formation of methane is largely reduced, as compared with gases containing less carbon monoxide, and the yield of the desired hydrocarbons containing more than one carbon atom in the molecule is increased as compared with gases containing more or less carbon monoxide.

It has already been proposed, in reactions carried out in the manner hitherto usual without the use of a liquid medium, to use gas mixtures of carbon monoxide and hydrogen in the ratio of from about 1:2 to 2:1 or even in wider ratios. For carrying out the process in practice, on a technical scale, however, only the reaction with gas mixtures rich in hydrogen, in particular those containing carbon monoxide and hydrogen in the ratio of 1:2, has been developed because when using a higher carbon monoxide content in the usual processes, the activity of the catalysts is impaired by the deposition of carbon black and consequently the reaction must be interrupted. Since many industrially important processes for the production of gases, such as the preparation of watergas, power gas or producer gas, yield gases containing as much carbon monoxide as, or more carbon monoxide than, hydrogen, a part of the carbon monoxide contained in the said industrial gases must be reacted with steam to give hydrogen in a special operation in order to carry out the processes in which, as hitherto usual, more hydrogen than carbon monoxide is employed for the conversion of these gases into hydrocarbons or their oxygen-containing derivatives, whereas in the present process in which an excess of carbon monoxide as compared with the amount of hydrogen is employed, the said conversion of the industrial gases in a special operation is not necessary.

The process according to the present invention, in which the reaction is carried out in the proper oil and with an initial gas containing 55—70 parts by volume of carbon monoxide to 45—30

[*Price* 1/-]

parts of hydrogen, offers the technical advantage that it is no longer necessary to react a large portion of the carbon monoxide present in the technical gases rich in carbon monoxide to yield hydrogen for the production of a suitable feed gas for the conversion into hydrocarbons and/or their derivatives containing oxygen.

The liquid medium led in a cycle may be led in the same direction as the reacting gases or in counter-current thereto. As in the process according to the said Specification No. 468,434 the proper oil used according to the present invention is one which contains considerable amounts of constituents which are gaseous or vaporous under the temperature and pressure conditions used. Since this temperature is preferably between 200° and 420° Centigrade the said gaseous or vaporous constituents consist at least to a large extent of those boiling within the boiling range of benzines.

The reaction may be carried out at atmospheric or increased pressure, as for example at 5, 20, 50, 100 to 300 atmospheres or more.

As catalysts there may be used all substances which accelerate in known manner the desired conversion into hydrocarbons and their oxygen containing derivatives, in particular those which cause the reaction to proceed according to the equation :—

$$2xCO + xH_2 = (CH_2)_x + CO_2$$

as for example catalysts containing iron as essential catalytic constituent.

It has been found that by using highly active iron catalysts, and gases rich in carbon monoxide according to the present invention, a working without troublesome deposition of carbon even under increased pressure and even when operating with a high throughput of such gases is rendered possible. The process may be carried out with advantage in two or more consecutive stages. For example the reaction of half of the mixture of carbon monoxide and hydrogen may be effected in the first stage, the remaining reaction being carried out in the second stage, if desired, after previous washing out of the carbon dioxide formed. Instead of carrying out the process in two stages, the residual gas (resulting after the removal of liquid products and carbon dioxide) may also be returned in a cycle to the first stage. Since according to the present invention, by reason of a far-reaching prevention of all side-reactions, the composition of the initial gas can be so rich in carbon monoxide (i.e. containing two volumes of carbon monoxide to one volume of hydrogen) that in the residual gas the components carbon monoxide and hydrogen are present in a substantially unchanged ratio and, in addition to the carbon dioxide formed, only small amounts of gaseous substances not participating in the reaction, such as methane, occur, the composition of the circulating gas feed from carbon dioxide undergoes no appreciable change as compared with the initial gas by the reaction.

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. The parts are by volume.

EXAMPLE.

A mixture of 1 kilogram of iron powder, 25 grams of silicon powder, 25 grams of titanium dioxide, 50 grams of potassium permanganate and 50 grams of water is fused in a current of oxygen, whereby the iron is converted into ferrosoferric oxide. The resulting melt, after cooling, is broken into pieces having a diameter of from about 6 to 8 millimetres and treated for 48 hours with hydrogen at 650° Centigrade. There then follows a further treatment for 36 hours with hydrogen at 500° Centigrade under a pressure of 75 atmospheres. The catalyst thus obtained is charged into a vertical high-pressure tube of 45 millimetres internal diameter and 0.08 metre in height in layers of about 1.5 centimetres in thickness at distances of 3 centimetres. The high-pressure tube is then charged with an oil boiling between about 50° and more than 300° Centigrade which has been obtained by a previous reaction according to the process hereinafter described.

0.13 cubic metre per hour of a gas containing 57 parts of carbon monoxide, 41 parts of hydrogen and 2 parts of nitrogen is led upwards through the tube which is heated to a temperature of 340° Centigrade and is kept under a pressure of 100 atmospheres. The gas flows through the tube and leaves it through a reflux condenser arranged vertically above the same. The oil formed in the tube and originally added is kept in the tube by the reflux condenser, an amount corresponding to the amount of oil formed being withdrawn.

The residual gas leaving the tube has the following composition :—

19.9	per cent. by volume of	CO_2
1.2	,,	gaseous olefinic hydro-carbons
37.3	,,	CO
33.9	,,	H_2
4.5	,,	gaseous paraffin hydro-carbons
3.2	,,	nitrogen.

0.76 cubic metre of residual gas leave the tube for each cubic metre of initial gas led in. In a single passage, 44 per cent. of the carbon monoxide and hydrogen are therefore brought into reaction. For each cubic metre of the mixture of carbon monoxide and hydrogen reacted there are formed 114 grams of oil, 33 grams of readily volatile hydrocarbons (propylene, butylene, pentene, propane and butane), 45 grams of gaseous hydrocarbons (methane, ethane and ethylene) and 650 grams of carbon dioxide. 39 per cent. of the oil boil up to 100°, 18 per cent. between 100° and 150°, 13 per cent. between 150° and 200°, 7 per cent. between 200° and 250°, 4 per cent. between 250° and 300°, and 19 per cent. above 300° Centigrade.

The said yield is maintained during operation for six months without any subsiding of the activity of the catalyst or any troublesome deposition of carbon.

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 reaction of carbon monoxide with hydrogen for the preparation of hydrocarbons or their oxygen-containing derivatives while using catalysts, at elevated temperatures and in a proper oil containing considerable amounts of constituents which are gaseous or vaporous under the temperature and pressure conditions used as described and claimed in the specification No. 468,434, which comprises starting from gas mixtures containing between 55 and 70 parts by volume of carbon monoxide to from 45 to 30 parts of hydrogen.

2. In the process as claimed in claim 1, working at a temperature between 200° and 420° Centigrade.

3. The process for the manufacture and production of hydrocarbons or their oxygen-containing derivatives substantially as described in the foregoing Example.

4. Hydrocarbons or their oxygen-containing derivatives when obtained by the process particularly described and ascertained.

Dated this 29th day of October, 1937.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

Reference has been directed, in pursuance of Section 8, sub-section (2), of the Patents and Designs Acts, 1907 to 1938, to Specification No. 468,434.

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