PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in the production of Hydrocarbons and Oxygen-Containing Organic Compounds from Carbon Monoxide and Water

We, BADISCHE ANILIN- & SODA-FABRIK, (I.G. Farben-industrie Aktiengesellschaft "In Auflosung"), a company registered under German Law, of Ludwigshafen/Rhein, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It has already been proposed to react carbon monoxide with water (instead of with hydrogen) to form organic compounds, such as hydrocarbons, alcohols, esters and acids. Such processes are of special interest for exploiting gases rich in carbon monoxide, as for example the waste gases from carbide furnaces or blast furnaces which are operated with oxygen.

In carrying out these processes it has been found that carbon black readily forms in the catalyst chamber. Furthermore there is frequently formed, by the contact of the carbon monoxide with the hot iron parts of the apparatus, iron carbonyl which may cause troublesome side reactions. This is especially the case when working at 300° to 400° C. under high pressure, as for example in the synthesis of methanol, isobutyl alcohol, isobutane or other branched hydrocarbons, or in synthese of hydrocarbons or oxygen-containing organic compounds, in particular alcohols, which are carried out under medium pressure (10 to 50 atmospheres). Furthermore a considerable part of the carbon monoxide reacts with steam with the formation of carbon dioxide and hydrogen.

We have now found that in processes for the production of hydrocarbons or oxygen-containing organic compounds by catalytic reaction of carbon monoxide and steam at elevated temperature the said drawbacks are substantially avoided when the gas leaving the reaction chamber, after complete or partial removal of the hydrocarbons or oxygen-containing organic compounds is returned to the reaction chamber, and the content of carbon dioxide in the circulating gas and/or the amount of water supplied are so regulated according to the equation of the watergas equilibrium $\frac{CO.H_2O}{CO_2.H_2}$ = constant that the gas leaving the reaction chamber contains substantially the same amount of hydrogen as the gas introduced into the reaction chamber.

During the reaction there is a tendency for watergas equilibrium to be set up according to the following equation:—

$$\frac{CO.H_2O}{CO_2.H_2} = \text{constant}$$

By adjusting a definite carbon dioxide content in the circulating gas and/or by appropriate measurement of the amount of water added, it is possible to ensure directly that the conditions characteristic of the process are maintained, i.e. that the hydrogen content in the circulating gas remains practically unchanged. The removal of carbon dioxide may be effected by washing the circulating gas with water under pressure and if desired also by cooling to such a low temperature that the carbon dioxide is liquefied. The purpose of the process is attained as a rule by regulating the carbon dioxide content in the circulating gas to about 2 to 10%.

In order to withdraw the heat of reaction it is advantageous to employ an amount of circulating gas which is considerably greater than the amount of fresh gas, for example 5 to 50 volumes of circulating gas to 1 volume of CO.

The remaining working conditions in the reaction of carbon monoxide with water differ according to the product which is to be prepared. As a rule temperatures of about 150° to 450° C. and pressures of 150 to 300 atmospheres or medium pressures of 5 to 50 atmospheres are used. The catalysts known for the syntheses of hydrocarbons and oxygen-containing organic compounds from carbon monoxide and water, as for example zinc oxide—chromium oxide, alkalised zinc-chromium oxide or thorium oxide together with aluminium oxide, for medium pressure syntheses especially iron catalysts, serve as the catalysts. The carbon monoxide concentration in the circulating gas preferably lies between 15 and 50% when methyl alcohol is to be prepared. For the production of isobutyl alcohol or of iso-hydrocarbons it may also be higher. The fresh gas, and also the steam, are preferably supplied at a point in the cycle where the gas has already been preheated by heat-exchange, for example shortly before the reaction vessel.

The following examples will further illustrate this invention but the invention is not restricted to these examples.

EXAMPLE 1.

Over 50 litres of a catalyst consisting of zinc oxide and chromium oxide and which has previously been reduced with hydrogen, there are led hourly at a pressure of 180 atmopheres and at a temperature of 380° C. 65 to 75 cubic metres of carbon monoxide and 35 to 40 kilograms of water. The gas leaving the reaction vessel is led in a cycle after removal of methyl alcohol, a speed of flow of 10000 litres per litre of catalyst per hour being maintained. A carbon dioxide content of about 2% is maintained in the circulating gas by washing with water under pressure. In this way the hydrogen content of the gas flowing through the reaction chamber is pratically unchanged. Both at the point of entry into the reaction chamber and at its exit therefrom it amounts to 51%. Besides this, the circulating gas contains 40% of carbon monoxide and 7% of nitrogen and methane. 30 to 35 kilograms of methyl alcohol having a specific gravity of 0.830 at 15° C. are obtained per hour.

EXAMPLE 2.

A gas containing carbon monoxide and steam in a molar ratio of 2.5 : 1 to 3 : 1 is passed over an alkalised iron-copper catalyst which had been reduced with hydrogen at from 280° to 290° C. together with 7 parts by volume of circulating gas (with reference to 3 parts by volume of the said gas mixture) at a temperature of 240° C. and a pressure of 12 atmospheres. The gas leaving the reaction chamber is stripped of carbon dioxide down to a content of from 3 to 5%, hydrocarbons and oxygenated products removed therefrom and the gas fed back into the reaction chamber. The hydrogen content set up in the circulating gas is from 30 to 35%. When it rises beyond this percentage, the hydrogen content is reduced again by decreasing the addition of steam, whereas the opposite measure is taken when the hydrogen content falls below the said percentage. 195 grams of hydrocarbons and small amounts of oxygenated products are obtained from each cubic metre of carbon monoxide charged in.

What we claim is:—

1. A process for the production of hydrocarbons or oxygen-containing organic compounds by the catalytic reaction of carbon monoxide with steam at elevated temperature characterised in returning the gas leaving the reaction chamber, after complete or partial removal of the hydrocarbons or oxygen-containing organic compounds, to the reaction chamber and adjusting the content or carbon dioxide in the circulating gas and/or the amount of water supplied according to the equation of the watergas equibrium $\frac{CO.H_2O}{CO_2.H_2}$ = constant so that the gas leaving the reaction chamber contains practically the same amount of hydrogen as the gas introduced into the reaction chamber.

2. The process for the production of hydrocarbons or oxygen-containing organic compounds substantially as described in either of the foregoing examples.

3. Hydrocarbons and oxygen-containing organic compounds when obtained by the process claimed in claim 1 or 2.

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