PATENT SPECIFICATION

738,652

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COMPLETE SPECIFICATION

Process for the Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German Company, and Lurgi Gesellschaft fuer Waermetechnik m.b.H., of Frankfurt am Main, Heddernheim, Germany, a German Company, 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 :—

The invention relates to a process for the hydrogenation of carbon monoxide, in which the products of the process have a high content of oxygen-containing organic compounds.

In the co-pending Patent Application No. 6839/51 (Serial No. 714,839), there is described and claimed a process for the synthesis of products having a high content of oxygen-containing organic compounds by the hydrogenation of carbon monoxide. The synethesis is effected by contacting a synthesis gas containing at least 1.2 volumes of hydrogen per volume of carbon monoxide, under synthesis conditions of temperature and pressure, with a precipitated iron catalyst containing one or more alkali-metal compounds (as hereinafter defined) in an amount of more than 5% by weight when calculated as K_2O and based on the total iron content of the catalyst, the catalyst being unsupported or containing not more than 20% by weight of supporting material relative to the total iron content and being used as a fixed bed or as a suspension in a liquid medium. The alkali-metal compounds which may be used in the catalyst in the process according to Specification No. 714,839 are those which exhibit an alkaline reaction, such as the hydroxides and carbonates, or those which are decomposed under synthesis conditions with the formation of alkaline-reacting compounds. Examples of the latter kind of alkali-metal compounds are the alkali-metal salts of many organic acids, such as the acetates and the oxalates. Alkali-metal halides and alkali-metal salts of non-volatile acids, for example, potassium fluoride, potassium silicate and potassium phosphate, are therefore not used to promote the catalyst in the process according to Specification No. 714,839.

It has now been found, according to the invention, that products having a high content of oxygen-containing organic compounds may be produced by a modification of the process claimed in Patent Specification No. 714,839, the modification consisting in the use of a synthesis gas which contains less than 1.2 volumes of hydrogen for every volume of carbon monoxide.

In many cases, the method of operation according to the invention has considerable advantages. On the one hand, the formation of methane and of C_2 hydrocarbons, which is generally undesirable, is markedly reduced. Moreover, the yield of high molecular weight compounds boiling in the range above approximately 320° C., is increased. Furthermore, a considerable increase in the quantity of esters is obtained, principally in the higher boiling range . These high molecular weight esters are particularly valuable for various technical purposes. After separation from the accompanying compounds, chiefly from the hydrocarbons, the esters may be further used as such. However, if it is desired to obtain larger quantities of high molecular weight alcohols, such alcohols may be easily obtained by saponifying the esters in known manner, for example, by the use of acids or of alkaline media, under normal or elevated pressure. The acid components in these esters have been found to be principally the radicals of acetic and propionic acids, so that alcohols may be obtained from the higher molecular weight esters, having about two to three fewer carbon atoms in the molecule than the esters. The use of gases rich in carbon monoxide is of particular

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importance because in the course of the development of modern processes for the production of gases from coal with the use of steam and oxygen, gases are formed from the outset which are relatively rich in carbon monoxide, the conversion of which into gases rich in hydrogen would be accompanied by losses.

The invention is illustrated in the following example.

EXAMPLE

An iron catalyst containing 100 parts of iron (Fe), 5 parts of copper (Cu), 10 parts of lime (CaO), and 10 parts of kieselguhr, was precipitated from a solution of the corresponding metal nitrates by means of a boiling solution of sodium carbonate. Upon completion of the precipitation, the *p*H was 9.2. The precipitated mass was immediately filtered in a filter press, and the filter cake was partially washed with distilled water (condensate water) to a residual alkali content of 8.4%, calculated as K_2O, relative to the total iron content. This partially washed mass was pre-dried to a residual water content of 60% H_2O and moulded into threads 3.5 mm thick, in a thread press. The moulded catalyst was then finally dried at a temperature of 110° C., broken into small pieces and screened through a sieve.

In a suitable reduction apparatus, this catalyst was reduced at a temperature of 310° C. with a gas mixture consisting of 75% hydrogen and 25% nitrogen, and with a linear gas velocity, calculated cold, of 1.20 metres per second. The duration of the reduction was 90 minutes. 70% of the iron in the catalyst was in the metallic state.

A gas consisting of 45% by volume of carbon monoxide, 43% by volume of hydrogen and 12% by volume of carbon dioxide, nitrogen and methane, was passed over this catalyst, in the manner described in Example 1 of the Patent Specification No. 714,839. At a temperature of 212° C., a conversion of 56% $CO + H_2$ was obtained. The methane formation and the formation of C_2 hydrocarbons decreased to approximately 8%, as compared with approximately 18% in the analogous method of operation with the synthesis gas used in the process described and claimed in Patent Specification No. 714,839.

Analysis of the liquid synthesis product showed that 27% of the synthesis product boiled above 320° C., as compared with 13% in the product obtained according to Example 1 of the main application. 40% of this 27% of high boiling products, were present in the form of high molecular weight esters from which, after saponification with an aqueous solution of potassium hydroxide, 35% were obtained in the form of high molecular weight alcohols.

What we claim is:—

1. In a process for the synthesis of products rich in oxygen-containing organic compounds as claimed in any one of Claims 1 and 3 to 19 of Patent Specification No. 714,839, the modification which comprises using a synthesis gas which contains less than 1.2 volumes of hydrogen per volume of carbon monoxide.

2. A process for the synthesis of products rich in oxygen-containing organic compounds, carried out with a carbon-monoxide-rich synthesis gas substantially as hereinbefore described.

3. A process for the hydrogenation of carbon monoxide using a synthesis gas rich in carbon monoxide, substantially as hereinbefore described in the example.

4. Synthesis products whenever obtained by the process of any one of the preceding claims.

EDWARD EVANS & CO.,
14—18 High Holborn, London, W.C.1,
Agents for the Applicants.

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