NOTE.—*The application for a Patent has become void.*
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PATENT SPECIFICATION

Convention Date (United States): Oct. 28, 1929. **371,804**

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Complete not Accepted.

COMPLETE SPECIFICATION.

Improvements in or relating to the Synthetic Production of Higher Alcohols.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W. 1, a Company registered under the laws of Great Britain, 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 relates to the catalytic synthesis of alcohols from hydrogen and an oxide of carbon and more particularly to the synthesis of higher homologues of methanol.

It is known that methanol, together with higher homologues thereof, can be synthesised by the passage of a gaseous mixture containing hydrogen and oxide of carbon at an elevated temperature and pressure over suitable catalysts. However, in spite of widespread technical interest in this field of organic synthesis and in spite of the present large commercial demand for the higher homologues of methanol, particularly for use in the manufacture of solvents for pyroxylin lacquers, there has been no known process for the economical synthesis of the higher alcohols. Such processes as have heretofore been proposed have suffered from the great practical disadvantage of producing along with the desired higher alcohols not only methanol but also methane and other gaseous hydrocarbons as well as aldehydes, ketones, tars and other undesirable and difficultly separable compounds. This difficulty of obtaining the desired products in a satisfactorily pure state, coupled with the inefficient utilization of raw materials in the production of relatively worthless by-products, has apparently been responsible for the fact that there has been no important commercial development of the synthesis.

It is the object of the present invention to provide a process whereby the practical synthesis of higher homologues of methanol may be effected by catalytic reaction of a gaseous mixture containing hydrogen and an oxide of carbon.

[*Price* 1/-]

Other objects and advantages of the invention will be apparent as it is better understood by reference to the following specification in which its details and preferred embodiments are described.

According to the present invention a process for the production of higher homologues of methanol comprises passing a gaseous mixture containing hydrogen and an oxide of carbon, the proportion of the latter not exceeding 10 per cent. by volume of the total mixture, over an alcohol-forming catalyst at a temperature exceeding 300° C. and under a pressure of at least 100 atmospheres.

Researches have shown that the problem of the practical synthesis of the higher alcohols referred to is dependent upon not one but a number of important factors and conditions without proper regard for which uneconomical results are obtained. More specifically it has been found that a careful selection of conditions of gas composition, pressure and temperature is essential to the effecient manufacture of a satisfactory product, quite apart from the specific catalyst employed. The present invention accordingly embodies a new method of operation involving a combination of certain specific and detailed conditions by virtue of the observance of which the practical and economical synthesis of higher alcohols is made possible.

It has been discovered, for example, that improved results may be obtained in the synthesis of higher homologues of methanol by subjecting to the action of a higher alcohol catalyst, at a temperature above 300° C. and a pressure in excess of 100 atmospheres, a gaseous mixture containing hydrogen and oxide of carbon, the latter being present in the gaseous mixture to the extent of less than 10% by volume. By operating in this manner it is possible to effect the synthesis of the higher homologues of methanol with an increased efficiency in consumption of raw materials and particularly with an improved quality of product.

It has also been found that apart from the conditions just stated improved results are secured by conducting the reaction with a catalyst of the general character above referred to, at a temperature over 300° C. and a pressure in excess of 100 atmospheres, with a gaseous reaction mixture containing hydrogen and oxide of carbon in a volume ratio exceeding 5 to 1.

It has been found that, regardless of other factors, an improvement is obtained in the efficiency of utilisation of raw materials and in the quality of product when a mixture of hydrogen and oxide of carbon is contacted with a higher alcohol catalyst at a temperature over 300° C. and a pressure above 100 atmospheres while regulating the reaction so as to provide in the gases leaving the catalyst only a relatively low proportion of oxide of carbon, which should not exceed 6% to 8% by volume. Preferably the oxide of carbon is not more than 2% to 4% by volume. The rate of flow of the gases is an important factor in attaining the desired low concentration of oxide of carbon in the gaseous products.

While the respective combinations of conditions above set forth are independently of importance, they may advantageously be used in combination one with another and it has in fact been found the best results are obtained when all the various conditions mentioned are simultaneously observed, that is, when a gaseous mixture containing hydrogen and oxide of carbon in a volume ratio exceeding 5 to 1 and containing less than 10% by volume of oxide of carbon, is contacted with a higher alcohol catalyst, at a temperature in excess of 300° and a pressure of over 100 atmospheres, while regulating the reaction to obtain a relatively low proportion of oxide of carbon in the exit gases. When these conditions are adhered to relatively little methane is formed and the condensate obtained upon cooling the hot gaseous products of the reaction contains, along with methanol, a mixture of the higher homologues thereof consisting largely of butanol and other alcohols of the series up to and including octanol. The product is characterised by a low content of very high-boiling alcohols and freedom from aldehydes, ketones, tars, resins, etc.

In its broadest aspect the invention is not limited to the use of any specific catalyst, higher alcohol catalysts, that is such catalysts as will produce substantial amounts of higher homologues of methanol from hydrogen and carbon oxide, being generally suitable. The catalysts used are preferably alcohol-forming catalysts containing at least one irreducible metallic oxide together with a relatively small amount of alkali metal oxide (preferably potassium). The term irreducible oxide is used here, and elsewhere in the specification and appended claims, in the sense in which it is generally applied in the alcohol synthesis art to those metallic oxides which are not substantially reduced to the metal under the conditions of the alcohol synthesis. The oxides of manganese, zinc, chromium and vanadium may be mentioned as examples. Reducible oxides, such as copper oxide, may also be present, if desired. Various oxides and mixtures thereof being known that may be used in the preparation of alcohol-forming catalysts, it is sufficient to indicate as examples of substances that may be employed in the present process, such catalysts as contain, in admixture or chemical combination, oxides of manganese, copper and potassium; zinc, chromium and potassium; chromium, manganese and potassium; copper, zinc and potassium; zinc, manganese and potassium; manganese, copper, chromium and potassium; etc. However, while as already pointed out the advantages of the specific operating conditions above set forth are not dependent upon the employment of any particular catalyst, practical trial has shown that when using the specific combinations of conditions stated the most satisfactory results, especially as regards quality of product, are produced, when the catalyst includes manganese oxide. Of the catalyst combinations that might be used, therefore, including those specifically named above, we preferably employ such as contain manganese oxide and an alkali metal oxide.

As indicative of the character of the product an analysis is given of the butanol and higher boiling fraction of the condensate, obtained commercially by the process herein described. For the purpose of comparison this analysis (Column A) is accompanied by a similar analysis (Column B), representing the best product obtainable hitherto by any known process. The percentages are by volume.

	A	B
Isobutanol - - - - -	65.9%	51.5%
Amyl, hexyl & heptyl alcohols - -	31.4%	16.0%
Very high boiling alcohols - -	2.7%	14.0%
Resins, tars, etc. -	none	18.5%

Gaseous mixtures of hydrogen and oxide of carbon from various sources may be employed in the process and the composition thereof may vary considerably providing the requirements previously specified are complied with. The gaseous mixture may, if desired, contain nitrogen, methane or other inert constituents. Thus, for example, suitably purified mixtures of hydrogen and carbon monoxide may be obtained from water-gas, coke oven gas, producer gas and the like, or by the catalytic reaction of carbon monoxide with steam or of gaseous hydrocarbons with steam and/or oxygen.

Although the specific method of practising the invention may be varied within wide limits for the purpose of illustration the following examples are given to indicate the manner of operating the process:

Example 1.

A catalyst containing manganese, copper, chromium and potassium may be prepared as follows:—To a dilute solution containing one mole of copper sulphate and two moles of manganese sulphate add a solution containing three moles of ammonium chromate. Add some ammonia to complete the precipitation. Wash the precipitate until practically free from ammonium sulphate, filter, and thoroughly mix the filter cake in a kneading machine with powdered potassium carbonate, the latter being employed in the proportion of 1 to 2% by weight of the total oxide in the mass. Dry the product at 300 to 400° C., crush it into particles of suitable size and reduce slowly with hydrogen at a temperature within the range of 100 to 300° C. In synthesizing higher alcohols, this catalyst was disposed in a reaction apparatus consisting of a nichrome tube of approximately 2/3" inside diameter, 1-3/8" outside diameter, and 24" length, provided with a closely fitting internal copper liner 1/32" in thickness. A copper clad steel thermocouple well, 1/4" outside diameter, was arranged axially in the tube. An annular catalyst layer 2" long was placed in the center of this tube, the remainder of the annular space being filled with pieces of fused silica. The apparatus was provided with electrical heating coils surrounding the entire length of the nichrome tube. A gaseous mixture containing about 75% by volume of hydrogen, 5% carbon monoxide and 20% nitrogen and other inerts, preliminarily freed from catalyst poisons, especially sulphur compounds, preferably free from oxygen and compressed to 900 atmospheres, was passed through the catalyst with the heating adjusted to maintain a temperature on the internal thermo-couple at the inlet edge of the catalyst bed of about 450° C., and with an inlet space velocity of about 60,000. Under these conditions the gaseous mixture leaving the catalyst, before condensation of liquefiable compounds, contained no more than about 1% CO. The gaseous products of the reaction were cooled under pressure to condense the liquefiable compounds which were separated by fractional distillation. A product of the general character indicated in Table A above was obtained.

Example 2.

A gaseous mixture, containing 80% by volume of hydrogen, 8% of carbonmonoxide and 12% of nitrogen and other inerts and free from substances deleterious to the catalyst, is passed at a pressure of 900 atmospheres over a catalyst prepared as follows: To a dilute solution containing one mole of zinc sulphate add a dilute solution containing one mole of ammonium bichromate, wash the precipitate by decantation until substantially free from sulphate, filter and dry at about 400° C. Moisten the dry material in a mixing machine with a solution of potassium chromate equivalent to 2% of the weight of the dry material. Again dry at above 125° C. and crush to suitable size, forming the crushed material, if necessary, into pellets or briquettes, and reduce the product slowly with hydrogen at a temperature within the range of 100—300° C. The catalyst is then disposed in the reaction apparatus and maintained at a temperature of about 450—525° C. while the aforementioned compressed gaseous mixture containing hydrogen and carbon monoxide is passed thereover at a space velocity of about 50,000. The effluent gases are subjected to cooling to condense the liquid products which are separated by fractional distillation.

No explanation or theory is offered as to the changes that may occur in the catalyst during either its preparation reduction or actual use, it being recognised that it is impossible to determine definitely the exact form or state in which the catalytic elements occur during the catalysis. Where, therefore, a metallic oxide is mentioned in the specification or claims as the constituent of a catalyst, this is to be understood as designating the metallic oxide as such or in any reduced, chemically combined or otherwise modified form in which it may be present during the catalysis.

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. Process for the production of higher homologues of methanol which comprises passing a gaseous mixture containing hydrogen and an oxide of carbon, the proportion of the latter not exceeding 10 per cent. by volume of the total mixture,

over an alcohol-forming catalyst at a temperature exceeding 300° C. and under a pressure of at least 100 atmospheres.

2. A process as claimed in claim 1 in which the initial gas mixture contains hydrogen and oxide of carbon in a volume ratio exceeding 5 to 1.

3. A process as claimed in claim 1 or 2 in which the gases are passed over the catalyst at such a rate that the proportion of oxide of carbon remaining in the gas after passage does not exceed 8 per cent.

4. A process as claimed in claim 3 in which the proportion of oxide of carbon remaining in the gas does not exceed 2 per cent.

5. A process as claimed in any of the preceding claims in which the catalyst employed comprises one or more irreducible oxides, together with an oxide of an alkali metal.

6. A process as claimed in claim 5 in which the catalyst employed comprises manganese oxide.

7. Process for the production of higher homologues of methanol substantially as described with reference to the examples in the accompanying specification.

8. Higher homologues of methanol whenever produced in accordance with the processes claimed in any of the preceding claims.

Dated the 23rd day of October, 1930.
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