PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Treatment of the Products of the Catalytic Conversion of Carbon Monoxide and Hydrogen

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen - Holten, Germany, a German Company, and LURGI GESELLSCHAFT FÜR WÄRMETECHNIK, m.b.H., Frankfurt a.M.-Haddernheim, 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 the treament of products obtained from the reaction of carbon monoxide with hydrogen at elevated pressures in the presence of catalysts.

In the synthesis of alcohols, and in given cases, hydrocarbons, by the conversion of carbon monoxide/hydrogen mixtures under elevated pressures of, for example, 5 atmospheres and higher, in the presence of catalysts which contain metals of the iron group and especially iron, or in the catalytic production of hydrocarbons and oxygen-containing by-products from carbon monoxide and hydrogen, mixtures of different groups of chemical compounds are obtained which have to be separated from each other and purified. The products so obtained suffer, in general, from a bad odour which is caused by a small content of unsaturated oxygen-containing compounds.

It is possible, by hydrogenation, to convert these unsaturated compounds into agreeably smelling saturated form and thereby obtain an improvement in the quality of the products. One disadvantage is, however, that a proportion of the olefins contained in the products of the synthesis is also hydrogenated at the same time, thus reducing the value of the products. The alcohols and the hydrocarbons are, however, generally separated from each other, the separation being effected in any suitable manner, for example, by solvent extraction or by azeotropic distillation. The above-mentioned disadvantage may, in this manner, be avoided. A proportion of the oxygen-containing impurities will, however, still remain in the hydrocarbon fraction. Their elimination from the hydrocarbon fraction is, in certain cases, required, and for this purpose one or several subsequent operations are necessary. For the following purposes, however, the hydrocarbons may be directly used after separation of the oxygen-containing organic compounds; as motor fuel, as feed to an OXO synthesis process, for oxidation, for sulphochlorination and the like.

Whichever the method of separation used, however, by far the larger proportion of the impurities will occur in the alcohol fraction. The alcohols are thereby rendered unsuitable for most uses by reason of the penetrating odour which characterises the impurities. Further measures for the purification of the alcohols are therefore required.

The removal of the oxygen-containing impurities with the alcohol component is not as such a disadvantage, but is, in fact, advantageous to the extent that by suitable reduction further alcohols are produced from these impurities. It has been demonstrated that with a suitably controlled reaction the alcohol yield is larger after the hydrogenation than before, the deleterious impurities disappearing at the same time.

According to the invention, therefore, the oxygen-containing organic compounds are separated from the synthesis product after which they are subjected to a mild hydrogenation. It is preferred to effect the separation by solvent extraction, extractive distillation or azeotropic distillation. The oxygen-containing organic compounds may, if desired, be separated from the extraction agent or agents before being subjected to hydrogenation, which hydrogenation is effected by means of hydrogen in the presence of catalysts. By this treatment the oxygen-containing impurities will lose their penetrating odour as they are converted into sweet-smelling substances consisting predominantly of alcohols. The term "mild hydrogenation" is used herein to identify a hydrogenation which leaves the alcohols, present in the fraction under treatment, substantially unaffected whilst malodorous oxygen-containing impurities are hydrogenated.

Various known extraction agents may be used for the extraction. Suitable extraction agents or solvents are, for example, methanol and its mixtures with water, ethanol, polyhydric alcohols such as glycol, glycerol, butanediol and the like; furthermore acetates, formates and the like. A single extraction agent may be used for the entire boiling range or the cut which is to be treated in accordance with the invention, the extraction being effected in one or more stages. On the other hand, two or more extraction agents may be used in two or more stages. Thus, for example, a synthesized alcohol-hydrocarbon mixture may be separated into fractions of boiling ranges 70° C.—180° C., 180° C.—220° C. and 220° C.—350° C., whereupon each of these fractions may be treated with a different extraction agent. Separation or removal of the extraction agent is then preferably effected by distillation in known manner. The extraction is advanageously carried out in counter-current manner. Upon removal of the extraction agent the extract, namely, the oxygen-containing compounds, is subjected to a mild hydrogenation. A copper-chromium oxide containing catalyst has proved to be particularly useful for this purpose. The hydrogenation is carried out at elevated pressure, such as, for example, 200 atmospheres and at a temperature at which the oxygen-containing impurities are just converted into alcohols without any alteration in the alcohols originally present in the mixture. Excellent results were obtained at a hydrogen pressure of 226 atmospheres and at a temperaure of 220° C. in the presence of a copper barium chromite catalyst prepared as set forth in United States Specifications Nos. 2,080,433 and 2,129,507.

The hydrogenation conditions vary with the nature and activity of the catalysts. In general, temperatures within the range 150°—270° C. and hydrogen pressures within the range 50—300 atmospheres are suitable, whilst temperatures within the range 200°—250° C. and hydrogen pressures of from 100 atmospheres to 250 atmospheres have been found to be particularly advantageous.

The preferred catalysts are those containing copper and chromium, particularly when the chromium is in the form of an oxide. Catalysts containing calcium oxide and/or barium oxide as well as those containing nickel, have also been found advantageous.

For the purpose of hydrogenation the materials to be treated may be passed over the catalyst in either vapour phase or liquid phase. When using relatively low boiling liquids vapour phase hydrogenation is frequently the better practice. It is also of advantage in some cases to dilute the substances to be hydrogenated with suitable solvents such as, for example, dioxane.

The hydrogen used in the hydrogenation may be drawn from the same source as the synthesis gas. On the other hand, it is possible to react the synthesis gas with steam in the presence of catalysts substantially in accordance with the equation $CO + H_2O = CO_2 + H_2$. The carbon dioxide is then removed, for example, by a water wash under pressure, and residual carbon monoxide is removed by a copper liquor wash and hydrogen under pressure is recovered in a substantially pure state. The hydrogen for the hydrogenation may also be obtained from the exit gases of the synthesis process. In this case, inert or deleterious gaseous components, such as carbon dioxide are eliminated from the exit gases, for example, by washing, after which the exit gases, if necessary, with the addition of steam, may be subjected to thermal decomposition to yield a mixture of carbon monoxide and hydrogen. This mixture is then converted to pure hydrogen in the above described manner and, after compression, the hydrogen is used in the hydrogenation step.

After the hydrogenation, the liquid fractions treated in accordance with the invention will contain surplus hydrogen, which hydrogen may be recovered. In many cases, it is advantageous to cool the liquid fractions before releasing the pressure for the recovery or separation of the hydrogen. The pressure may be released in stages, thus permitting the hydrogen to be returned to the process in a partly compressed form.

Aqueous solutions produced during synthesis may also be treated in a similar manner, as for example, by separating the alcohols by distillation from their aqueous solution or by extracting the aqueous solution with substanially water-insoluble, preferably oxygen-containing, solvents, and thereafter to subject the extract, preferably after removal of the solvent therefrom, or the water-free distillate, as the case may be, to a mild hydrogenation. Essentially only alcohols are obtained in this manner instead of the mixtures of aldehydes and the like, which are still present together with the alcohols and which can only be treated with difficulty. The treatment in accordance with the invention of the mixture obtained from the aqueous reaction material may be also effected together with the alcohols isolated from the water-insoluble synthesis product.

The process of the invention is illustrated by the following examples:—

EXAMPLE 1.

A water gas having been substantially freed in known manner from sulphur compounds, resin-forming materials and other deleterious substances, and containing carbon monoxide and hydrogen in a ratio of 1:1.1 by volume was passed at a pressure of 26 atmospheres over a catalyst obtained by melting pure iron with additions of 2.5% Al_2O_3 and 0.4% K_2O and thereafter activated by reduction in a stream of hydrogen. The synthesis temperature used was 182° C. with a space velocity of 120 volumes of gas per volume of catalyst per hour. The products of the synthesis were cooled and the condensate formed separated into an oil layer and an aqueous layer. The oil layer was subjected to distillation and the fraction boiling between 135° C. and 380° C. was recovered. The fraction contained on the average 52% alcohols together with about 0.3% acids, 4.6% esters and 2.5% aldehydes and ketones, the remainder of the fraction comprising essentially hydrocarbons. The fraction was then extracted with methanol. A continuous seven-stage countercurrent extractor was used, to which the mixture to be extracted was added from one side, methanol being added from the other side. Four parts by volume of methanol were used for each part by volume of the alcohol-containing separation into layers and in order to increase the selectivity, small amounts of fraction. For the purpose of obtaining water were added to the methanol during the course of the seven-stage extraction. The quantities of water added during the extractions are given in the following table:—

TABLE.

Stage	1	2	3	4	5	6	7
Volume % of water added, calculated on methanol	0.2	0.3	0.4	0.4	0.7	0.7	0.9

The operational temperature was 20° C. The extract of oxygen-containing organic compounds was distilled. The extract, freed in this manner from the solvent, contained about 95%—99% of the oxygen-containing organic compounds present in the oil layer of the synthesis product. About 80% of the non-alcoholic oxygen-containing compounds were present in the extract.

This extract together with hydrogen under a pressure of 121 atmospheres was passed over a hydrogenation contact catalyst prepared in accordance with the procedure set forth for a copper barium chromite in U.S. Specifications Nos. 2,089,433 and 2,129,507. The utilizable catalyst layer was about 2 metres high and was maintained at a temperature of 220° C. The liquid and the hydrogen were both used in preheated condition and were both passed downwardly through the catalyst.

After cooling of the mixture withdrawn from the bottom and separation of the liquid, the hydrogen was recycled to the hydrogenation stage. The persistent and somewhat pungent odour had disappeared and the products from the hydrogenation stage possessed an agreeable aroma. Analysis showed that the aldehydes and ketones had substantially disappeared and that the esters had been practically completely converted into alcohols. A reduction in alcohol content could not be established.

By fractionation and distillaion the alcohols were then obtained in a substantially pure condition. The alcohols so obtained may be used for practically any purpose. Thus they may be used in the perfumery and food industries; for example, as anti-foaming agents in the production of jam.

EXAMPLE 2.

A highly purified water-gas of the composition specified in Example 1 was used in a synthesis process in accordance with the procedure set forth in that example. In this case, however, the synthesis was carried out at a pressure of 31 atmospheres and the catalyst used was one obtained in known manner by precipitation from an appropriate solution to yield an iron catalyst containing 1.3% Al_2O_3 and 0.3% Na_2O.

The oily products obtained in the synthesis were then distilled for the recovery of a fraction of boiling range 170° C.—220° C. This fraction contained approximately 60% alcohols, 0.5% organic acids, 2.5% esters and 3% aldehydes and ketones. The fraction was then extracted in accordance with the invention with about three times its volume of methanol, the methanol containing 2.5% of water. The extraction was carried out in a seven-stage extraction centrifuge described in U.S. Specifications Nos. 2,036,924 and Re. 21168. In this manner the alcohols contained in the fraction were recovered to the extent of about 97% whilst the other oxygen-containing organic compounds were recovered to the extent of about 85%. After removal of the methanol and water, the extract, in vapour form, in admixture with hydrogen which was under pressure of 181 atmospheres, was passed to the hydrogenation stage as set forth in Example 1. The catalyst used was a copper barium chromite catalyst possessing the same composition as specified in Example 1. In the present case, however, the catalyst was used in pelleted form. The gaseous mixture was maintained in contact with the catalyst for a period of about 40 minutes. The reaction temperature was maintained at 230° C. The gaseous products from the hydrogenation zone were cooled in order to liquefy the condensible materials therein.

Results showed that the hydrogenation did not only fail to produce any loss of alcohols but that the yield of alcohols was in fact increased by the hydrogenation from about 60% to 63.8%, calculated on the synthesis product. Alcohols were therefore produced by the conversion of other oxygen-containing compounds originally present in the treated fraction. The characteristic and pungent odour possessed by this fraction was removed by the hydrogenation.

EXAMPLE 3.

Highly purified water gas obtained as specified in Example 1 and of the same composition was passed, at a pressure of 400 lbs. per square inch gauge and at a temperature of 600° F., through a substantially vertically arranged column type reaction vessel. An iron catalyst was provided in this reactor, the catalyst consisting of pulverized FE_3O_4 with small additions of Na_2CO_3. The gas, with the catalyst in suspension, was introduced in turbulent flow at the foot of the column. The major portion of the catalyst, together with the gas, passed out of the upper part of the reactor. The catalyst was separated from the gas in known manner and was recycled to the foot of the reaction zone for admixture with the gas entering the column.

The so-called Hydrocol process operating according to the principles of the "fluidized" synthesis furnishes in addition to hydrocarbons which may, for example, be used for motor fuel or the like, an aqueous component including valuable oxgen-containing organic compounds. These may be separated by distillation and can be obtained in reasonably pure form. They do however possess an unpleasant odour, which hinders their use in many directions. This disadvantage may be removed in accordance with the invention in the following manner:—

The aqueous portion of the synthesis product was subjected to distillation in a distillation apparatus of the double column type. In the first column system the water of reaction was substantially freed from all organic compounds by the injection of direct steam. These compounds are obtained as an azeotropic mixture with water and may be largely separated from the distillation water by separation into two layers. The one layer comprises the distillation water in solution equilibrium with the organic substances and is returned to the distillation column. The other layer comprises the water-saturated mixture of the organic distillation components and in the second column system it is freed in known manner from its water by azeotropic distillation using, for example, benzene as carrier for the water.

The water-free bottoms product of the second column was composed of about 52% alcohols, 10% aldehydes, 10% ketones and 28% acids. This mixture was then subjected to hydrogenation at a hydrogen pressure of 151 atmospheres and a temperature of 230° C. The hydrogenation was effected in an autoclave provided with a stirrer, being continued therein for a total period of time of about 30 minutes. Hydrogen was passed into the autoclave at the rate at which it was used up in the hydrogenation reaction. In the course of the hydrogenation practically all of the aldehydes and acids were converted into alcohols, while the ketones were only changed or modified to a minor extent. All of the products were of excellent quality and could be obtained in substantially pure form by distillation in known manner.

EXAMPLE 4.

The same fraction of the oily synthesis products specified in Example 2 and boiling within the range 170° C.—220° C., was used. The oxygen-containing organic compounds were separated from the fraction by azeotropic distillation. This was carried out by distilling the fraction in a distillation column with butylene glycol (1,3). The residual oxygen-containing organic compounds were then removed from the bottom of the distillation column while the hydrocarbons were present in the distillate, having distilled over in the form of an azeotropic mixture with the butylene glycol. The yield of organic oxygen-containing compounds was 87%. The oxygen-containing compounds, having been first freed by washing with water from a small amount of butylene glycol, were then treated in the manner specified in Example 2, the same good results being obtained.

EXAMPLE 5.

In this instance, also, a fraction boiling between 170° C. and 220° C. of the products of a carbon monoxide hydrogenation to hydrocarbons and alcohols, was used. The hydrocarbons and the oxygen-containing organic compounds of this fraction were separated by extraction of the vapour mixture in a distillation column with a α-naphthylamine, the naphthylamine being added in the liquid state at the top of the column. The mixture forming at the bottom of the column consisted substantially of oxygen-containing organic compounds and α-naphthylamine. The mixture was withdrawn from the column and subjected to distillation for removal of the oxygen-containing organic compounds. The yield was 91%. The further treatment was conducted in the manner specified in Example 4.

What we claim is:—

1. A process for the treatment of the products of the conversion of carbon monoxide and hydrogen into alcohols and hydrocarbons under elevated pressure in the presence of an iron-containing catalyst, which comprises separating oxygen-containing organic compounds from the products, or a fraction of the products, and subjecting the oxygen-containing organic compounds to a mild hydrogenation.

2. A process according to claim 1, in which the mild hydrogenation is effected in the presence of a catalyst at a temperature within the range 150° C.—270° C., and at a hydrogen pressure within the range 50—300 atmospheres.

3. A process according to claim 2, in which the temperature is within the range 200° C.—250° C., and the hydrogen pressure is within the range—250 atmospheres.

4. A process according to claim 2 or claim 3, in which the caalyst contains at least one member of the group consisting of copper, chromium, chromium oxide, barium oxide and nickel.

5. A process according to any of the preceding claims, in which the oxygen-containing organic compounds are separated by solvent extraction, extractive distillation or azeotropic distillation.

6. A process according to claim 5, in which the extraction agent or agents are separated from the oxygen-containing organic compounds before the latter compounds are subjected to the mild hydrogenation.

7. A process for the separation and treatment of oxygen-containing organic compounds obtained in the products of the reaction of carbon monoxide with hydrogen, substantially as described in any of Examples 1 to 5.

8. A process for the separation and treatment of oxygen-containing organic compounds obtained in the products of the reaction of carbon monoxide with hydrogen, substantially as hereinbefore described.

9. Oxygen - containing organic compounds whenever obtained by the process of any preceding claim.

Dated this 9th day of August, 1950.
EDWARD EVANS & CO.,
14—18, High Holborn, London, W.C.1,
Agents for the Applicants.

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ERRATA

SPECIFICATION NO. 688,778

Page 3, line 55, *after* "alcohol-containing" *insert* "fraction. For the purpose of obtaining".

Page 3, *delete* line 58.

Page 3, line 104, *for* "distillaion" *read* "distillation".

Page 5, line 71, *for* "range -250" *read* "range 100-250".

THE PATENT OFFICE,
9th April, 1953

DB 28029/1(12)/3409 100 4/53 R

m.b.H., Frankfurt a.M.-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:—

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