PATENT SPECIFICATION

702,595

Date of Application and filing Complete Specification July 3, 1950.
No. 16559/50.
Application made in Germany on July 23, 1949.
Complete Specification Published Jan. 20, 1954.

Index at acceptance :—**Class 32,** A2(B : D : G2).

COMPLETE SPECIFICATION

Improvements relating to the Separation of Oxygen-Containing Organic Compounds from Aliphatic Hydrocarbons by Distillation

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German Joint-Stock 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 separation of aliphatic alcohols and other oxygen-containing organic compounds from their mixtures with aliphatic hydrocarbons.

It is an object of the invention to provide a process of separation based on azeotropic distillation of the mixture which results in the isolation of a major proportion of the oxygen-containing organic compounds, particularly of the alcohols.

It is a further object of the invention to provide means whereby higher molecular alcohols can be separated from mixtures with aliphatic hydrocarbons such as are obtained in the catalytic hydrogenation of carbon monoxide.

Oxygen-containing organic compounds and more particularly higher alcohols have been recovered from their mixture with aliphatic hydrocarbons in various ways. Thus selective extraction with certain solvents, amongst them aniline, glycol and nitrobenzene, enables oxygen-containing organic compounds, and more especially alcohols, to be separated from mixtures with hydrocarbons such as are formed, for example, in the catalytic hydrogenation of carbon monoxide. Another way of effecting such a separation is by fractional adsorption of oxygen-containing organic compounds on activated Fuller's earth or aluminium hydroxide. A third way of isolating oxygen-containing organic compounds consists in subjecting the mixtures as a whole to an alkali fusion, whereby the alcohols which form approximately 90% of the oxygen-containing organic compounds present in the mixtures obtained as products in the catalytic hydrogenation of carbon monoxide, are converted almost completely into salts of fatty acids (soaps) which can easily be isolated, for example, by separation into layers.

All these known processes involve the drawback of requiring a rather involved mode of operation.

It has now been found that it is possible to effect in a simple manner involving azeotropic distillation a practically complete separation of alcohols in a pure state from such mixtures, accompanied by a partial separation of other oxygen-containing compounds. The method of effecting the separation according to the invention, consists in adding to the mixture or a fraction of the mixture to be treated an alcohol diluted with water, the added alcohol being one which contains fewer carbon atoms in the molecule than any alcohol present in the mixture or fraction to which it is added and being one which forms ternary azeotropic mixtures with the water and the aliphatic hydrocarbons in the mixture or fraction to which it is added. The mixture or fraction to which the water and alcohol have been added is then subjected to distillation, and an azeotropic mixture or mixtures of hydrocarbons, added alcohol and water distils over, whereupon the alcohols and other oxygen-containing compounds which remain in the residue, can be separated from each other by distillation, if necessary *in vacuo*, or by other known methods.

The mixture or fraction to which the water and alcohol are added, is preferably one which consists only of compounds in which the difference between the number of carbon atoms in the compound or compounds containing the least number of carbon atoms in the molecule and the compound or compounds containing the greatest number of carbon atoms in the molecule, is at least two but is not greater

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than six. Thus if the compounds containing the least number of carbon atoms in the molecule are C_5 compounds, then it is preferred that the mixture or fraction to which the alcohol and water are added should be at least a C_5—C_7 fraction but should not be wider than a C_5—C_{11} fraction.

It is preferred that the final boiling point of the mixture or fraction to which the water and alcohol are added, should not be higher than 250° C.

In the process according to the invention the aliphatic hydrocarbons present in the mixture, after the alcohol and water have been added, form during distillation ternary azeotropic mixtures which boil at materially lower temperatures than the oxygen-containing compounds which thus remain in the residue. In this manner substantially complete separation of the aliphatic hydrocarbons is obtained, in contrast to the method of ordinary distillation, where the hydrocarbons tend to distil over with the alcohols and other oxygen-containing organic compounds present.

It has been found that propanol is particularly suitable for use as the added alcohol. It is preferred to use propanol recovered from the products of the hydrogenation of carbon monoxide.

When the azeotropic mixture or mixtures of hydrocarbons, added alcohol and water, are condensed, two layers are formed, the upper layer consisting almost entirely of the distilled hydrocarbons. This layer may be separated by overflow. If the upper layer should contain small quantities of the added alcohol, for example propanol, the alcohol may be separated from it by fractional distillation. The added alcohol thus separated may be returned to the step of azeotropic distillation.

The hydrocarbons in the upper layer of the azeotropic condensate may be freed of their content of alcohol by means other than distillation. Thus the layer may be treated with water. This step of washing with water is preferably effected in countercurrent.

The lower aqueous layer of the condensate contains, besides water, only the added alcohol, and consists, for example, of aqueous propyl alcohol. This aqueous layer is returned into the distillation column used in the treatment of the initial mixture or fraction, to be subjected again to azeotropic distillation.

After the hydrocarbons have completely distilled over in the form of azeotropically boiling ternary mixtures, a binary mixture of water and added alcohol, for example aqueous propyl alcohol, finally distils over. The boiling temperature then rises sharply. This phenomenon indicates that the residue still present in the distillation column practically consists of oxygen-containing organic compounds and in the main of alcohols. When this residue is itself distilled under normal elevated or lowered pressure, the alcohols present in it are recovered in the order of their molecular weights and in a high state of purity. Instead of or in addition to subjecting the residue to distillation, it may also be subjected to selective extraction or to fusion with alkali or to some other known and suitable method of separation or extraction.

When mixtures consisting of aliphatic and substantially straight-chain hydrocarbons and oxygen-containing organic compounds are treated in accordance with the process of the invention the hydrocarbons may also be separated according to the number of carbon atoms in their molecules, for the boiling points of the ternary mixtures rise with the increase in the number of carbon atoms in the hydrocarbons. Thus, by means of a highly efficient fractionating column separation into fractions containing hydrocarbons having substantially the same number of carbon atoms in the molecule is possible.

Apart from products of the catalytic hydrogenation of carbon monoxide, the process of the invention is also well adapted for treating other mixtures of hydrocarbons with oxygen-containing organic compounds resulting from industrial processes, such as, for example, the catalytic addition of mixtures of carbon monoxide and hydrogen to olefines. Similar mixtures are also obtained in the working-up petroleum products and in other catalytic processes. Similar mixtures are also sometimes present in naturally ocurring raw materials and in the products of their conversion.

The following examples illustrate the process of the invention.

EXAMPLE 1

A fraction boiling in the range 110°—160° C., obtained in the hydrogenation of carbon monoxide at a pressure of 20 kg/sq.cm. in the presence of an iron catalyst, was mixed with about 25% by volume of propyl alcohol diluted with 28% water and the mixture then distilled. In three fractions, ternary mixtures passed over at 81° C., 85 C° and 88° C. respectively. In these fractions C_8-, C_9- and C_{10}- hydrocarbons, respectively, predominated. After completion of the azeotropic distillation of the hydrocarbons, the aqueous propyl alcohol still present distilled over in the form of a binary mixture at a temperature above 88° C. At the end of this operation the boiling temperature rose considerably.

From the residue remaining after the azeotropic distillation had come to an end, C_4-, C_5- and C_6- alcohols were separated in a satisfactory state of purity by simple distillation.

EXAMPLE 2

From the products of the hydrogenation of carbon monoxide effected in the presence of an iron catalyst at a pressure of about 15 kg/sq.cm. a primary fraction boiling in the range 160°—204° C. was separated. This fraction had the following characteristics:—

Neutralization number - = 2.2
Iodine number - - - - - = 35
Hydroxyl number - - - - = 250
Carbonyl number - - - - = 12
Ester number - - - - - = 16.5

It is seen from these characteristics that the fraction contained appreciable quantities of unsaturated hydrocarbons, aldehydes and esters. Furthermore, the neutralization number shows that small quantities of acids were also present in the fraction.

25% by volume of aqueous propanol containing approximately 70% of propanol, was added to the fraction and the mixture was distilled. The ternary azeotropic mixtures which distilled over were condensed; the hydrocarbon layer of the condensate contained about 5% of propanol. This layer was separated from the lower aqueous layer of the condensate and, in a separate column, was freed from the propanol which was returned to the azeotropic distillation process. The quantity of hydrocarbons thus obtained constituted 30% by volume of the original primary fraction.

At the end of the azeotropic distillation of the hydrocarbons, a residue remained from which C_7-, C_8- and C_9- alcohols were recovered in a high state of purity by distillation *in vacuo*.

What we claim is:—

1. A process for the separation of aliphatic alcohols and other oxygen-containing organic compounds from their mixtures with aliphatic hydrocarbons which comprises adding water and an alcohol to the mixture, the added alcohol being one which contains fewer carbon atoms in the molecule than any alcohol in the mixture and forms ternary azeotropic mixtures with the water and the hydrocarbons, and subjecting the aqueous mixtures so formed to distillation to yield a distillate consisting of hydrocarbons, water and added alcohol and a residue rich in oxygen-containing organic compounds.

2. A process for the separation of aliphatic alcohols and other oxygen-containing organic compounds from aliphatic hydrocarbons in a mixture obtained as product in the catalytic hydrogenation of carbon monoxide, which comprises distilling the mixture to yield two or more fractions, adding water and an alcohol to one of the fractions, the added alcohol being one which contains fewer carbon atoms in the molecule than any alcohol in the fraction and which forms ternary azeotropic mixtures with the water and the hydrocarbons in the fraction, and thereafter distilling the fraction to yield a distillate consisting of hydrocarbons, water and added alcohol and a residue rich in oxygen-containing organic compounds.

3. A process according to Claim 1 or Claim 2, in which the mixture or fraction to which the water and alcohol are added consists only of compounds in which the difference between the number of carbon atoms in the compound containing the least number of carbon atoms in the molecule and the compound containing the greatest number of carbon atoms in the molecule, is at least two but is not greater than six.

4. A process according to any one of the preceding claims, in which no compound present in the mixture or fraction to which the water and alcohol are added contains less than four carbon atoms in the molecule.

5. A process according to any one of the preceding claims, in which the added alcohol is a monohydric aliphatic alcohol.

6. A process according to any one of the preceding claims, in which the added alcohol is propanol.

7. A process according to any one of the preceding claims, in which the residue is subjected to distillation for the recovery and separation of the individual oxygen-containing organic compounds.

8. A process according to any one of the preceding claims, in which the azeotropic mixtures which distil over are condensed and allowed to settle, the upper, hydrocarbon-containing layer, which separates on settlement being then freed of its content of alcohol.

9. A process according to Claim 8, in which the upper, hydrocarbon-containing layer is freed from its content of alcohol by distillation.

10. A process according to Claim 8, in which the upper, hydrocarbon-containing layer is freed from its content of alcohol by washing it with water in countercurrent flow.

11. A process according to Claim 8, in

which the lower layer, comprising an aqueous solution of the added alcohol, which separates on settlement, is returned to the step of azeotropic distillation.

12. A process substantially as described with reference to Example 1.

13. A process substantially as described with reference to Example 2.

14. A process for the separation and recovery of oxygen-containing organic compounds contained in the products of the process of catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described.

15. A process for the separation of aliphatic alcohols from their mixtures with aliphatic hydrocarbons, substantially as hereinbefore described.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1954.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.