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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the Selective Extraction of Oxygen-containing organic compounds from their mixtures with aliphatic hydrocarbons

We, Ruhrchemie Aktiengesellschaft, of Oberhausen-Holten, Germany, a German joint-stock Corporation, 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:—

The invention relates to a process for the selective extraction of oxygen-containing organic compounds from their mixtures with aliphatic hydrocarbons.

It is known that during the process of catalytic hydrogenation of carbon monoxide, not only hydrocarbons but also oxygen-containing compounds, such for example as alcohols, aldehydes, acids, esters, ketones and acetals, are formed. When iron catalysts are used such oxygen-containing compounds are produced in particularly large quantities. Hydrocarbons and compounds containing oxygen are also formed during other chemical processes, for example, during the reaction of adding water-gas to unsaturated hydrocarbons, or during the oxidation of paraffins. Furthermore, hydrocarbon compounds of other origin sometimes contain oxygen compounds in considerable quantities.

In many cases separation of the oxygen compounds is desirable, for they are frequently valuable by-products commanding high prices. In other cases the hydrocarbons in question cannot be used in further production processes, particularly where they are produced from carbon monoxide and hydrogen, if the compounds containing oxygen are not first removed.

It has already been suggested catalytically to convert the oxygen compounds or to destroy them in order to prevent them from hindering the treatment of the hydrocarbons in further processes. By such processes the valuable oxygen-containing compounds are lost, which loss is considerable where large quantities of the oxygen-containing compounds are present.

Selective adsorption of the oxygen-containing compounds on activated silicic acid, alumina or other adsorption media has been attempted. Such processes have met with little success.

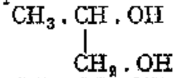
It has been found that oxygen-containing organic compounds may be satisfactorily separated in a simple manner from aliphatic hydrocarbons, particularly from the primary products obtained by the hydrogenation of carbon monoxide in the presence of an iron catalyst, by selective solvent extraction, if the mixtures are treated with a polyhydric alcohol, an aromatic nitro-compound, an aromatic amino compound or an oxygen compound of the furan group, which extraction media are liquid under the conditions of the extraction.

The term "oxygen compounds of the furan group," as used in the specification and the appended claims, is to be understood as including the following compounds:—furan, furfural, the partially and completely hydrogenated derivatives of furan and of furfural, and the alkyl derivatives of furan and of furfural.

Suitable extractive media are, for example, glycol, glycerine, aniline, nitrobenzene, furfurol or their alkyl derivatives. Mixtures of these compounds can also be used. The compounds referred to and their alkyl derivatives only dissolve hydrocarbons to a small degree, whilst oxygen-containing compounds are adequately dissolved.

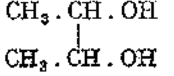
Particularly well suited for the extraction of oxygen-containing compounds from aliphatic hydrocarbons are polyhydric alcohols, as hydrocarbons are practically insoluble in polyhydric alcohols. In addition to the simple polyhydric alcohols their homologues can also be used, for example:—

monomethyl glycol ..



$$\begin{array}{l} CH_3 . CH . OH \\ \qquad\ | \\ \quad\ \ CH_2 . OH \end{array}$$

dimethyl glycol ..



$$\begin{array}{l} CH_3 . CH . OH \\ \qquad\ | \\ CH_3 . CH . OH \end{array}$$

or trimethylene glycol.

[Price 2s. 8d.]

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The selective effect of the extractive media of the invention may sometimes be improved by the addition of a small quantity of water, up to 10% by volume of the solution.

If it is desired to extract large quantities of oxygen-containing compounds of high molecular weight from admixture with aliphatic hydrocarbons, the solvent power of polyhydric alcohols is sometimes inadequate. In such instances it is advantageous to add to the polyhydric alcohol, for example glycol, small quantities of monohydric alcohols of low molecular weight, for example methyl alcohol or ethyl alcohol. By such means the absorption capacity of the glycol for high molecular oxygen-containing compounds is considerably increased. It is particularly advantageous to mix with the glycol a fraction of 50° C.–70° C. boiling range obtained by fractionation of the products produced in the catalytic hydrogenation of carbon monoxide in the presence of iron or cobalt catalysts. This process has the advantage that for the extraction and working up of the oxygen-containing compounds no extraneous compounds beyond the polyhydric alcohols are used. The fraction of 50° C.–70° C. boiling range may also be used in admixture with the other extractive media.

For carrying the process of the invention into effect, the mixtures to be treated are caused to flow through extraction towers arranged in cascade or series. The extraction towers are advantageously provided with suitable distributors and/or packing in order to ensure adequate contact and mixture with the solvent. In this manner, from an aliphatic hydrocarbon mixture having an OH figure of 90–100 and a CO figure of 8–10 and containing small quantities of other oxygen compounds, all the oxygen products were extracted through a four-stage process to yield an end product at the last stage which did not show any OH figure or a CO figure. For the removal of the last traces of the polyhydric alcohols used as extraction media and the lower molecular weight monohydric alcohols that may have been added, for example methyl alcohol, a subsequent water treatment of the hydrocarbon compounds is advantageous.

The separation of the extracted oxygen-containing compounds from the extraction media such, for example, as glycol, is effected by simple distillation. In so far as no constant boiling azeotropic mixtures are formed, the individual oxygen-containing products are obtained directly in a state of high purity in the order of their boiling points. The oxygen-containing compounds lying above the boiling points of the extraction media, for example, above the boiling point of glycol, are advantageously separated by vacuum distillation in order to prevent decomposition and polymerisation.

The invention is illustrated, but in no way limited, by the following examples.

EXAMPLE 1

Four extraction towers were arranged in series, each tower having a volume of 800 cc and being packed with Raschig rings of 5 mm diameter, and containing 700 cc of glycol. 200 cc per hour of a primary product of the catalytic hydrogenation of carbon monoxide were passed through the system. The hydrocarbon mixture had an initial boiling point of about 60° C. and a final boiling point of about 500° C. at atmospheric pressure. Its OH figure was 120. The hydrocarbon mixture was passed into each extraction tower through a distributor plate fixed at the base of the tower. Owing to its lower specific gravity it passed upwards through the glycol and was drawn off through an overflow pipe to pass to the next extraction stage. The hydrocarbon mixture from the first extraction tower still possessed an OH-figure of 24. After the second extraction stage this figure was OH-15. The hydrocarbon mixture from the last extraction tower had an OH-figure of about only 1–2.

EXAMPLE 2

A two-stage extraction process had in each stage a volume of 800 cc and a packing of porous sintered plates ("Frittenplatten"). The first tower was filled with pure glycol, whilst the second tower contained a mixture of equal parts of glycol and methyl alcohol. 150 cc per hour of a product of hydrogenation of carbon monoxide were passed through the extraction towers, the product having an OH-figure of 90 and an initial boiling point of 135° C. The hydrocarbon mixture was led into the lower part of the first extraction tower and taken off from the upper part of that tower and then passed into the lower part of the second extraction tower and finally withdrawn from the upper part of the second tower. The hydrocarbon mixture was then washed with water in order to remove the glycol and methyl alcohol. It then had an OH-figure of only 13.

EXAMPLE 3

In known manner, water-gas was added to an olefin-containing hydrocarbon fraction having a boiling range of 150°–220° C. obtained by the thermal cracking of petroleum, the addition of the water-gas being effected under super-atmospheric pressure and at elevated temperature in the presence of a cobalt catalyst. Subsequent hydrogenation with the same catalyst at a still higher temperature converted the aldehydes produced into the corresponding alcohols. The end product so obtained contained 35%

alcohols, 5% olefines and 60% saturated hydrocarbons.

For the extraction of the alcohols obtained the mixture was treated in the apparatus described in Example 1. The first extraction tower contained pure glycol, the second was filled with a mixture containing 2 parts of glycol and one part of methyl alcohol. The third tower was charged with a mixture that contained glycol and methyl alcohol in equal parts. The last tower contained water in order to remove the glycol and the methyl alcohol from the treated mixture.

In this manner about 80% of the alcohols present were separated from the treated mixture and were obtained in a practically pure state.

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. A process for the selective extraction of oxygen-containing organic compounds from their mixtures with aliphatic hydrocarbons, particularly from the primary products obtained by the hydrogenation of carbon monoxide in the presence of iron catalysts, in which the mixtures are treated with a polyhydric alcohol, an aromatic nitro-compound, an aromatic amino-compound, or an oxygen compound of the furan group, as hereinbefore defined, under such extraction conditions that the extractive media are liquid.

2. A process according to claim 1, in which monohydric alcohols of low molecular weight are used in admixture with the polyhydric alcohols.

3. A process according to claim 1 or claim 2, in which water is added to the polyhydric alcohols in an amount up to 10% by volume of the solution so produced.

4. A process according to any one of the preceding claims, in which the polyhydric alcohol is a dihydric alcohol.

5. A process according to claim 4, in which the dihydric alcohol is glycol.

6. A process according to any of the preceding claims, in which the extractive medium is diluted with a fraction of boiling range 50° C.–70° C. derived directly from the products obtained in the hydrogenation of carbon monoxide over iron or cobalt catalysts.

7. A process for the extraction of oxygen-containing organic compounds from their mixtures with aliphatic hydrocarbons, in which the mixtures are treated with a liquid solvent consisting of two or more compounds selected from the following groups:—polyhydric alcohols, aromatic nitro-compounds, aromatic amino-compounds and oxygen compounds of the furan group as hereinbefore defined.

8. A process for the selective extraction of oxygen-containing compounds from mixtures containing aliphatic hydrocarbons, particularly from the primary products obtained by the hydrogenation of carbon monoxide, substantially as hereinbefore described.

9. A process for the selective extraction of oxygen-containing compounds from their mixtures with aliphatic hydrocarbons, substantially as hereinbefore described with reference to any of Examples 1 to 3.

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

Dated this 18th day of June, 1949.
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London, W.C.1.
Agents for the Applicants.

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