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COMPLETE SPECIFICATION

Process for the Separation of Oxygenated Aliphatic Compounds from Mixtures thereof with Hydrocarbons

We, RUHRCHEMIE AKTIENGESELLSCHAFT, a German Company, of Oberhausen-Holten, Germany, and Lurgi Gesellschaft für Wärmetechnik m.b.H., a German Company of Frankfurt a.Main-Heddernheim, Germany, 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 separation of oxygen-containing aliphatic compounds from mixtures of such compounds with hydrocarbons.

It is known to use selective solvents for the separation of oxygenated aliphatic compounds, such as alcohols, esters, acids, aldehydes, ketones and the like, from mixtures of such compounds with aliphatic hydrocarbons, such as paraffins and olefins. Glycol, glycol derivatives, aliphatic alcohols, furfural and aniline are examples of substances which have been proposed as solvents of this kind; the solvent may comprise a mixture of two or more of such substances or an aqueous solution of such a substance. Methyl alcohol has particularly frequently been suggested for this purpose because it exhibits greater selectivity than higher molecular weight aliphatic alcohols, that is to say, it dissolves the oxygenated compounds well but dissolves hydrocarbons only to a small extent. In particular, methyl alcohol and, in individual cases, ethyl alcohol have been successfully used for the processing of primary products from carbon monoxide hydrogenation containing a high proportion of oxygenated compounds. In the case of the use of methyl alcohol the addition of water in amounts of as much as about 20% by volume based on the methyl alcohol, has been proposed in order to increase the selectivity. Also, a two-stage extraction of mixtures of this kind has been proposed, with the use of methyl alcohol which had been diluted with water in the first stage and a concentrated methyl alcohol as the extracting agent in the second stage. Although no precise information as to the proportion by volume of the mixture to be extracted to the extraction medium appears to be given in the literature, the ratio in most cases varies from about 1:3 to 1:7.

It is an object of the invention to provide a process for the separation of oxygenated aliphatic compounds, particularly alcohols, from mixtures of such compounds with hydrocarbons which contain more than 40% by weight of the oxygenated compounds by extraction in stages with aqueous methanol or ethanol solutions, whereby both the low molecular weight and the higher molecular weight oxygenated compounds may be recovered in a state of high purity and in an almost quantitative yield.

According to the invention, a process for the separation of oxygen-containing aliphatic compounds from a mixture of such compounds and hydrocarbons containing more than 40% by weight of the oxygen-containing compounds, comprises subjecting the mixture to solvent extraction in at least three stages with about an equal volume of aqueous ethanol in each stage, the water content of the solvent used in the first stage being from 40% to 70% by volume, the water content of the solvent used in the second stage being from 10% to 30% by volume, and the water content of the solvent used in the third stage being not in excess of 20% by volume.

According to the invention furthermore, a process for the separation of oxygen-containing aliphatic compounds, particularly alcohols, from a mixture of such compounds and hydrocarbons containing more than 40% by weight of the oxygen-containing compounds, comprises contacting the mixture with aqueous methanol in at least three extraction stages, the ratio by volume of the mixture to the solvent in each stage being about 1:1, the water content of the solvent used in the first stage being from 40% to 60% by volume, the water content of the solvent used in the second stage being from 10% to 20% by volume, and the water content of the solvent used in the third stage being not in excess of 10% by volume.

The preferred solvent is aqueous methanol. In the first stage of extraction, the aqueous methanol preferably has a water content of 50%-55% by volume, in the second stage the aqueous methanol preferably has a water content of 15%-20% by volume, whilst in the third stage the water content of the methanol is preferably about 5% by volume.

When aqueous ethanol is employed as the solvent, the water content of the solvent in the first stage is preferably not less than 45%, the water content of the solvent in the second stage is preferably not less than 15%.

The method of operation in accordance with the invention is based on the finding that the opinion frequently maintained that, for the quantitative recovery of the higher molecular weight alcohols (particularly those containing more than 8 carbon atoms in the molecule) from the mixtures, the presence of the low molecular weight oxygenated compounds in the alcohols used as solvents, that is to say, the methanol or ethanol in the present case, would be advantageous, is not correct in accordance with the results obtained. It has surprisingly been found that by maintaining certain operating conditions as for example, with respect to the number of extraction stages, the water content of the methyl alcohol in the individual stages, the ratio of methyl alcohol to total mixture to be extracted and to the mixture to be extracted in the individual stages, and frequently also the cross-sectional load in the extraction columns, and the like, particularly advantageous extraction results are obtained in accordance with the invention if the low molecular weight oxygenated compounds are first removed as extensively as possible by means of aqueous methanol which is relatively rich in water. After and not before this step, an extraction of the higher molecular weight oxygenated compounds should be effected with the use of high-percentage methyl alcohol.

A ratio by volume of mixture to be extracted to solvent of about 1:1 in the first stage gives the best results. Particularly advantageous results were obtained when at the same time a cross-sectional load in, for example, columns packed with Raschig rings of a diameter of about 5 mm-20 mm. and preferably about 5 mm-10 mm., of about 4-7 cubic metres total liquid per square metre of cross-section of the column per hour was maintained. Other extraction methods such, for example, as those employing mixing or centrifugal pumps are also suitable for carrying out the process according to the invention. The extraction itself is suitably effected in counter-current flow relationship. With the use of aqueous methyl alcohol as the solvent, the water content of the solvent in the first stage should be within the range of 40%-60% by volume and is advantageously within the range 50%-55% by volume. By operating in this manner, the low molecular weight alcohols containing up to 4 or 5 carbon atoms in the molecule, together with any other oxygenated compounds containing the same number of carbon atoms in the molecule, are extensively removed in the first stage. By far the greater part of the higher molecular weight alcohols remains in the raffinate of the first stage.

The raffinate from the first stage is then again extracted with a less dilute methyl alcohol, the extraction being likewise effected with a ratio by volume of raffinate to solvent of about 1:1 and, when using packed columns, with the same or similar cross-sectional load of the column. It has been found that with mixtures which contain 50%-65% of oxygenated compounds a methanol concentration in the second stage of about 90%, that is a water content of about 10%, is the most suitable. If, however, the concentration of oxygenated compounds is in excess of 65%, the second stage is preferably carried out with methanol of a concentration of about 80%-85% (that is, 15%-20% by volume of water). Although a large proportion of the higher molecular weight oxygenated compounds is extracted in this stage, a quantitative recovery is not achieved after the second stage. A subsequent extraction in a third, and, for specific conditions, in a fourth and fifth stage is required to achieve a substantially complete separation of the oxygenated compounds from the hydrocarbons.

If the separation of mixtures containing about 50%-65% of oxygenated compounds is involved, a third extraction stage will generally be sufficient in which likewise a ratio by volume of raffinate to methanol or ethanol of about 1:1 is used to obtain a quantitative separation. In this case, the methanol solvent used in the third stage should have a concentration of 90%-100% and preferably of 95%, that is, it should contain only 0%-10% of water. If, however, the content of oxygenated compounds in the initial mixture is higher as for example, in excess of 65%, an alcohol of about 90% by volume (that is, 10% of water) is used in the third extraction stage and a subsequent extraction is effected under the same conditions in a fourth, and, if necessary or desired, even in a fifth stage with a 90%-100% and preferably 95% methanol. In this manner not only is a practically quantitative recovery of the higher molecular weight alcohols possible, but these alcohols are, after removal of the solvent by distillation, obtained in a state of high purity, namely above 90% and frequently even of 95%-98% purity.

When ethyl alcohol is used in place of methyl alcohol, the water content of the ethyl alcohol, due to its lower selectivity, should always be higher than that of the methyl alcohol. In the first two extraction stages this additional water content should constitute about 5%-10% by volume while 2%-5% by volume are sufficient in the following extraction stages.

The particular and decisive importance of the process in accordance with the invention lies in its application to such liquids as the liquid primary products of the hydrogenation of catalytic carbon monoxide, which contain more than 40% by weight and preferably more than 55% by weight of oxygenated compounds. By far the best results have been obtained with such a product where about 45%-75% by weight of the liquid product boils between 30°C. and 180°C., while 18%-28% by weight boils between 180°C. and 320°C. and 8%-30% by weight boils above 320°C.

In addition to the simple method of operation, the quantitative separation of the oxygenated compounds and the high degree of purity obtainable, the manner of operation in accordance with the invention has the advantage that the amount of methanol required is extremely low as compared with the amount required in methods hitherto known. This is not unimportant for economic reasons since with the use of large quantities of methanol, this methyl alcohol must be separated by distillation which, due to the high latent heat of vaporisation of methyl alcohol, involves the use of a considerable amount of power. Corresponding to the preferred manner of operation in accordance with the invention with its low methanol requirement, the steam and energy requirement is only a fraction of that required in known processes, namely about 15%-25%. This is understandable when it is considered that the ratio of mixture to be extracted to methanol and in the preferred manner of operation in accordance with the invention, and in contrast to practically all known processes is only about 1:1 to 1:1.5.

The invention is illustrated by the following Examples.

EXAMPLE 1.

Water gas was passed at a synthesis pressure of 10 atmospheres and a catalyst load or space velocity of 150 litres of gas per litre of catalyst per hour over a precipitated, reduced iron catalyst which contained 5 parts of copper, 10 parts of CaO and 10 parts of kieselguhr per 100 parts of iron and which also contained, as promoter, 8% of an alkali metal compound (incorporated in the catalyst as K_2CO_3) calculated at K_2O and based on the total iron content, 70% of the total iron content of the catalyst being in the metallic state. The recycle ratio was 1:2.5 and the reaction temperature was 218°C.

The resulting primary product (without the reaction water) had the following boiling ranges: above 320°C., 14%; 180°C.-320°C., 25%; 30°C.-180°C., 61%. About 55% by weight of oxygenated compounds were present in this product.

The total primary product excluding the heavy constituents obtained in the hot separator, that is less than the 14% mentioned above, was charged to the extraction process. Of course, small amounts (about 2%) of heavy constituents boiling above 320°C. were present in the diesel oil fraction (180°C.-320°C.).

This product was intermittently saponified under pressure in a small saponification column in batches of 5 kg. each in such manner that the quantity of reaction water formed in the synthesis per 5 kg. of total primary products (including paraffin) was first added, whereupon a quantity of solid KOH, which had been calculated from the neutralization number and saponification number of the quantities of water and oil, plus an excess of 20% of the theoretical amount was added. The saponification was effected at 145°C., under a pressure of 9 atmospheres for a period of 45 minutes.

The reaction product obtained was separated in a receiver. While the aqueous phase was processed by distillation to give the corresponding alcohols, the upper phase which was now practically free from acids and esters and consisted chiefly of alcohols and small amounts of aldehydes and ketones, was passed to the extraction process.

The extraction column consisted of a glass tube of 25 mm. inside diameter containing a packing of ceramic material (Raschig rings 5 × 5 mm.). The effective length of the extraction column was 1100 mm. Three of these columns were used, one for each stage.

25 litres (about 20 kg. with approximately 10% of water) of the above primary product were extracted with 25 litres of 50% methanol (about 22.2 kg.) at room temperature. The throughput was about 1200 cc./hr. of both saponified primary product and methanol. The primary product was introduced at the lower end of the column while the aqueous methyl alcohol was introduced at the top of the extraction column. After about 21 hours, the extraction was terminated. 31.2 kg. of extract 1 (methanol phase) and 10.8 kg. of raffinate 1 (hydrocarbon phase) were obtained.

The 10.8 kg. of raffinate, having a volume of 13,850 cc., from the first stage were passed to the second stage which was operated in the same manner with respect to load and method of flow during the extraction. The methyl alcohol now used (13,850 cc.) had a concentration of 89%, the remainder being water. The duration of the extraction was about 11 hours.

The result from the second stage was an extract 2 of 21.7 litres corresponding to 17.4 kg. and a raffinate 2 having a volume of 5.3 litres and a weight of 4.02 kg.

The raffinate from the second stage (4.02 kg. = 5.3 litres) was again extracted in the third stage under the same conditions with 92% by volume of methanol (5.3 litres). The extraction time was about 4.5 hours. An extract 3 (6.4 litres = 5.3 kg.) and a raffinate 3 (4 litres = 3 kg.) were obtained. The processing of the three extracts and of the raffinate 3 showed that, based on the total alcohols in the C_6-C_{14} range, the proportion of residual alcohol of each individual carbon number in the raffinate 3 was between about 0.1% (C_6-C_8) and 1.5% (C_{12}-C_{14}). The quantities of alcohol obtained by distillation from the three extracts, based on total alcohol of each individual carbon number, were practically 100% for carbon numbers of up to 10 (C_{10}) and about 98.5% to 99% for carbon numbers of between 11 and 14 (C_{11}-C_{14}). The purity of the alcohols extracted was from 93% to 95%.

Processing of the three methanol extracts by distillation showed also that between 30° and about 60°C., a binary mixture which consisted chiefly of low boiling hydrocarbons and methanol distilled over. This mixture separated in the cold state into two layers. The upper lay which consisted practically only of hydrocarbons was analysed and a total quantity of 4.5 kg. of low boiling hydrocarbons was found.

Despite the great number of manipulations, the losses were relatively low.

EXAMPLE 2

A quantity of the total primary product (including the heavy constituents boiling above 320°C.) obtained in the synthesis described in Example 1, was charged to the extraction process without previous saponification. To prevent clogging by solid materials, the extraction was effected in a small pressure column at temperatures of about 50°C. The column had the same dimensions and packing as the column of Example 1, but consisted of iron. The feeding of the methanol stream and of the primary product stream was effected by means of small pressure pumps. The load during the extraction, which was also operated in this case in three stages, was of the same order of magnitude as that used in Example 1.

Processing of the three extracts by distillation showed that up to a boiling point of about 300°C., the quantity of oxygenated compounds extracted (alcohols, aldehydes, ketones, esters and acids) was 97%, based on total oxygenated compounds present. The degree of purity varied between 91% and 96%.

The oxygenated compounds present in the heavy constituents boiling above 320°C. and consisting substantially of esters (ester content of the constituents boiling above 320°C.;—about 45%) could not be completely extracted. The degree of extraction was about 70% based on the total ester content present, and the purity of the esters obtained by distillation was 80% to 85%.

What we claim is:—

1. A process for the separation of oxygen-containing aliphatic compounds from a mixture of such compounds and hydrocarbons containing more than 40% by weight of the oxygen-containing compounds, which comprises subjecting the mixture to solvent extraction in at least three stages with about an equal volume of aqueous ethanol in each stage, the water content of the solvent used in the first stage being from 40% to 70% by volume, the water content of the solvent used in the second stage being from 10% to 30% by volume, and the water content of the solvent used in the third stage being not in excess of 20% by volume.

2. A process for the separation of oxygen-containing aliphatic compounds, particularly alcohols, from a mixture of such compounds and hydrocarbons containing more than 40% by weight of the oxygen-containing compounds, which comprises contacting the mixture with aqueous methanol in at least three extraction stages, the ratio by volume of the mixture to the solvent in each stage being about 1:1, the water content of the solvent used in the first stage being from 40% to 60% by volume, the water content of the solvent used in the second stage being from 10% to 20% by volume, and the water content of the solvent used in the third stage being not in excess of 10% by volume.

3. A process according to Claim 2, in which the water content of the solvent used in the first stage is from 50% to 55%, the water content of the solvent used in the second stage is from 15% to 20% and the water content of the solvent used in the third stage is about 5%.

4. A process according to Claim 2 or Claim 3, in which more than three extraction stages are used, the water content of the solvent used in the fourth stage and any subsequent stage being from 0-10% and being preferably about 5%.

5. A process according to Claim 1, in which four or more extraction stages are used with aqueous ethanol as the solvent, the water content of the solvent used in the

fourth stage and any subsequent stage being not more than 15%.

6. A process according to any one of the preceding claims, in which the mixture contains more than 55% by weight of oxygen-containing aliphatic compounds.

7. A process according to any one of the preceding claims, in which the mixture of oxygen-containing aliphatic compounds and hydrocarbon being treated is derived from the products obtained by the catalytic hydrogenation of carbon monoxide.

8. A process according to any one of the preceding claims, in which the mixture contains more than 65% by weight of oxygen-containing aliphatic compounds, and the extraction is effected in four or five stages.

9. A process according to any of Claims 1 to 6, in which the mixture is derived from the liquid primary product of the catalytic hydrogenation of carbon monoxide, 45%-75% by weight of which primary product boils in the range 30°C.-180°C., 18%-24% by weight boils in the range 180°C.-320°C. and 8%-30% by weight boils above 320°C.

10. A process according to any one of the preceding claims, in which the extraction is effected countercurrently in packed columns.

11. A process according to Claim 10, in which the loading of each column is from 4 to 7 cubic metres of total liquid per square metre of the cross-sectional area of the column.

12. A process for the separation of an oxygen-containing aliphatic compound from a mixture of such compounds and hydrocarbons containing more than 40% by weight of the oxygen-containing compounds, which consists in extracting the mixture with aqueous methanol or aqueous ethanol in at least three extraction stages substantially as hereinbefore described.

13. A method of separation of oxygen-containing aliphatic compounds from mixtures of such compounds and hydrocarbons containing more than 40% by weight of the oxygen-containing compounds, substantially as hereinbefore described with reference to Example 1 or Example 2.

14. Oxygen-containing aliphatic compounds and hydrocarbons whenever obtained by the process claimed in 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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